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Selection and Evaluation of Sorbent Resins for the Collection of Organic Compounds

Arthur D Little, Inc, Cambridge, Mass

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SELECTION AND EVALUATION OF SORBENT RESINS FOR THE COLLECTION OF ORGANIC COMPOUNDS

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16. ABSTRACT The report gives results of an experimental program to characterize the behavior of resins which can be used in the sorbent trap module of a sampling train used for environmental assessment studies. Experimental design considerations were based on the sorbent canister in the new source assessment sampling system (SASS) train. Both XAD-2 and Tenax-GC resins were studied. Investigated compounds represented both a regular homologous series and compounds of direct interest to shipboard incineration studies. Two experimental approaches were used: a gas chromatography method using elution analysis to determine volumetric capacity (Vg) at low pollutant concentrations; and a steady state apparatus for frontal analysis to determine weight capacities of the resins. The studies showed that XAD-2 has a greater volumetric and weight capacity than Tenax-GC and is, therefore, preferred for use in the SASS train sorbent canister. A regular relationship was observed between the capacity of the resin and the volatility of the compounds studied. Under normal SASS train sampling conditions, materials such as POMs, PCBs, and Agent Orange would be completely retained by either the XAD-2 or Tenax-GC resin.

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SUMMARY

An experimental program has been conducted to characterize the behavior of resins which can be used in the sorbent trap module of a sampling train used for environmental assessment studies. Experimental design considerations were based on the sorbent canister in the new source assessment sampling system (SASS) train. Both XAD-2 and Tenax-GC resins were studied. Compounds were chosen for investigation which represented both a regular homologous series and compounds of direct interest to shipboard incineration studies.

Two experimental approaches were used: one a gas chromatography method using elution analysis for the determination of volumetric capacity (Vg) at low pollutant concentrations, and the other a steady state apparatus for frontal analysis to determine the weight capacities of the resins.

The studies showed that XAD-2 has a greater volumetric and weight capacity than Tenax-GC and is, therefore, preferred for use in the SASS train sorbent canister. A regular relationship was observed between the capacity of the resin and the volatility of the compounds studied.

Under normal SASS train sampling conditions, materials such as polynuclear aromatic hydrocarbons, polychlorinated biphenyls and Agent Orange would be completely retained by either the XAD-2 or Tenax-GC resin. However, at higher pollutant levels the use of XAD-2 with its greater weight capacity would be necessary. Neither resin efficiently retains volatile materials such as vinyl chloride monomer.

I. INTRODUCTION

The new source assessment sampling system (SASS) train includes a sorbent trap module designed to collect volatile materials which pass through the high efficiency glass fiber filter.[1] The sorbent trap module consists of a gas conditioner designed to cool the gas stream to 60°C*, followed by a canister containing a macroreticular organic resin for the collection of volatile organic compounds and any other species, such as volatile metals, which may have the correct properties for collection on the resin. The sorbent canister is followed by a receiver to collect the water and other liquids which condense and pass through the resin.

Recent studies[2,3] have shown sorbent traps of this type to have good characteristics for the recovery and analysis of organics from pollution sources. However, very little systematic quantitative data have been obtained which are directly applicable to the design conditions of the SASS train sorbent module. The purpose of this task was to initiate studies which would characterize the quantitative behavior of the sorbent trap. In particular, a series of shipboard incinerator tests are to be conducted, and it was desirable to know the behavior on the sorbent module of the materials to be burned in these tests. Initial interests in connection with the incinerator tests included the following compounds:

Selected polynuclear aromatic hydrocarbons (POM's)
Selected polychlorinated biphenyls (PCB's)
Vinyl chloride monomer
Agent Orange (2,4-D and 2,4,5-T)
2,3,7,8 tetrachlorodibenzo-p-dioxin

At the time this task was initiated (April 1976), Tenax-GC had been selected as the resin for the sorbent trap, based upon the behavior of this material from POM collection.[2] However, other studies which had examined a broader range of pollutants[3,4] indicated that the resin XAD-2 would be a better choice of material for the full range of compounds to be encountered in the environmental assessment studies. In late April 1976, Arthur D. Little, Inc. had prepared a background discussion on some of the factors affecting the selection of sorbent trap resins for the collection of organic compounds.[5] The factors presented in that discussion are important to an understanding of the behavior of these resins in the collection of organic compounds and in understanding the reasons for preferring the use of XAD-2 resin. Because that discussion was not prepared as a report for distribution, it has been incorporated in the "Background" section of this report. It is hoped that inclusion of this more general discussion will aid in understanding the various choices that are available in designing a system for the collection of organic vapors and the basic mechanisms operating in the use of sorbent traps.

* The design temperature of 60°C at the time of these studies has since been lowered to 20°C.

Many factors affect the collection efficiency and capacity of sorbents for chemical species. Some of these are:

Sorbent surface area
Sorbent pore volume
Sorbent specific adsorptivity
Pollutant vapor pressure (volatility)
Pollutant concentration
Gas flow rate
Sampling temperature
Gas stream moisture
Presence of other pollutants

A complete evaluation of all of these factors was beyond the scope or time available for this task. Rather than attempt to examine each of these factors in detail, data from the previous studies were used to design a program which made it possible to obtain basic data directly relevant to the incineration tests.

The use of a conventional sampling train for all of the studies required for this program would have been prohibitively time-consuming and would also have posed difficult problems in studying hazardous materials. In addition, from analysis of the physical properties of many of the compounds of interest (e.g., PCB's, Agent Orange), it was not expected to be able to directly measure their collection efficiency and breakthrough because of their high boiling points. The program approach was designed to

1). test the collection behavior of compounds as a function of some readily measurable parameter, such as boiling point, and

2). evaluate a rapid screening approach based upon a gas chromatograph (GC) type experiment.

Studies have been completed for a number of compounds on both the Tenax-GC and XAD-2 resins. This report presents the research findings using both the conditions of a conventional sampling train and the GC approach.

II. BACKGROUND

A. Previous Sorbent Studies

The material in this BACKGROUND section was reported in a preliminary form in April, 1976.[5] The purpose of this section is to present a brief discussion of the alternatives in selecting resins for use in sorbent traps such as those currently in use in modified Method 5 trains and the new SASS train. While Tenax-GC is currently in use in several such trains, the use of XAD-2 resin has been favored in studies conducted by Arthur D. Little, Inc. (ADL) except where thermal stability is an issue. Unfortunately, complete studies on all of the characteristics which should be evaluated for both resins have not yet been done for either one. The preferences are derived from experience at ADL with these materials over the last four years and a recent comparative evaluation of XAD-2 and Tenax-GC for an EPA incinerator performance evaluation program.[4]

The use of such materials as charcoal, silica gel, GC column packings (silicones on supports), etc. for the collection of trace materials has been known and practiced for many years. These previous studies have led to the recognition of serious deficiencies in many of these materials. While charcoal has tremendous collection efficiency and capacity, quantitative recovery for analytical purposes has been poor. Silica gel is useful in some cases but has serious limitations in humid environments. Other materials show selectivity in collection and have low capacities.

Dravnieks[6] was probably one of the first to systematically evaluate macroreticular resins for use in collecting trace ambient pollutants. In 1972, ADL began the routine use of Chromosorb 102 in the collection of diesel exhaust organic pollutants for work on the diesel odor problem.[7] Chromosorb 102 was selected at that time after comparison with Chromosorb 101, silica gel and charcoal. Chromosorb 102 has since been used on many similar sampling problems with complete success. Battelle Columbus Laboratories (BCL) were also beginning to evaluate these resins in about 1972-73. (Personal Communications) Emphasis at BCL was on techniques for direct GC interfacing and, thus, thermal desorption. Tenax-GC was, therefore, selected as a preferred substrate for that approach. The emphasis at ADL was on solvent desorption methods (pentane), and the Chromosorb 102 performed well in that regard. Zlatkis' work on the use of Tenax-GC for these purposes was first published in 1973.[8]

Thus, there is a fortuitous situation where two different sorbent media have been selected, each optimized and satisfactory for the particular studies to which they were applied. In the following sections, an attempt has been made to present the information currently (and conveniently) available on a comparative evaluation of the two basically different types of resins.

B. Available Sorbent Resins

No attempt has been made to determine all sorbents which may be available and appropriate for these purposes. The ones considered are those which others have found useful and, particularly, those which do not have strong selectivity characteristics. Resins commonly considered are:

Chromosorb 101	Johns-Manville
Chromosorb 102	Johns-Manville
XAD-2	Rohm and Haas
XAD-4	Rohm and Haas
Tenax-GC	Enka N.V.
Poropak series	Waters Associates

C. Physical Properties

Several basic parameters are important in selecting substrates for gas phase adsorption. Besides the chemical surface properties, the physical parameters are:

particle size	range and distribution
pore volume	mean and distribution
surface area	total and distribution

The particle size will affect the pressure drop across the adsorbent bed and will also determine whether mass transfer from the gas phase to the particle will be rate limiting and thus affect the collection efficiency. Within a given adsorbent, the pore volume and surface area are interrelated. A larger surface area will usually lead to greater equilibrium adsorption capacity, but the surface must be available within the time allowed in the bed transport. Thus, adsorbents which have lower surface areas are sometimes more effective because they have a larger amount of surface available in large pores, where gas phase diffusion will not be rate limiting.

Some of the physical properties of these resins are given in Table 1. Initial purchase costs are also given for comparison, but none of these reflect final use cost, since each resin must be cleaned before using. The significance of some of these differences in properties will be further explained in the next section where performance testing is discussed.

Whereas most of the previous ADL studies had been done using Chromosorb 102, the XAD resins were evaluated because they were available in a larger mesh size range and thus could have a lower pressure drop in a sampling train. It is understood that Chromosorb 102 and XAD-2 are virtually identical chemically, both being a divinylbenzene cross-linked polystyrene. Tenax-GC is a polyphenylene oxide.

Table 1

Physical Properties of Sorbent Media

Sorbent	Mesh Size	Bulk Density (g/cc)	BET Surface Area (m^2/g)	Pore Volume (cc/g)	Purchase Price ($/g)
Chromosorb 101	-	-	approx. 30	-	-
Chromosorb 102	40 - 80[a]	0.36	374	0.829	0.24
XAD-2	20 - 50	0.38	350	0.854	0.0088
XAD-4	20 - 50	0.38	925	1.145	0.013
Tenax-GC	35 - 60[b]	0.14	25	0.053	3.2

a. largest size range available, sold as 60 - 80

b. 60 - 80 mesh is also available

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Based upon the observed mesh size data for these materials, the pressure drop across a packed bed should increase in the order XAD < Tenax-GC < Chromosorb.

The density of Tenax-GC is about one-third that of the other resins.

The surface areas of Chromosorb 102 and XAD-2 are about the same, XAD-4 is three times that of XAD-2, and the Tenax-GC surface area is only one-fourteenth that of XAD-2. Thus, XAD-4 might be expected to have the highest equilibrium capacity and Tenax-GC the least. The pore volumes reflect the surface area data.

The distribution, and thus availability, of the surface area is an important consideration. In Figures 1 - 4 the surface area distribution is shown as a function of pore volume respectively for Tenax-GC, Chromosorb 102, XAD-2 and XAD-4. Nearly all of the Tenax-GC surface area is in very small sized pores, < 40A. Chromosorb 102 and XAD-2 have very similar patterns with a good portion of their area in 200 - 300 A pores and the balance in pores < 50A. XAD-4 has no area in large pores, but all in pores < 90A.

From these data and previous filtration experience, Chromosorb 102 and XAD-2 would be expected to be the most efficient resins for collection at the flow rates of the SASS train.

As is shown later in this section, XAD-4 does have the greatest collection capacity, but it has been difficult to quantitatively recover material from this resin. Presumably, the small pores greatly increase the time required for diffusion in solvent extraction methods.

In a source assessment train sampling hot gases, thermal stability of the resins is an important issue. Tenax-GC is known to have superior properties in this respect. We have examined Chromosorb 102, XAD-2 and Tenax-GC by thermal analyis methods, obtaining differential scanning calorimetry (DSC) traces and thermogravimetric analysis (TGA) curves in an air atmosphere. These are shown in Figures 5a-c (DSC) and 6a-c (TGA).

From the DSC traces the resins appear thermally stable up to

Chromosorb 102	200°C
XAD-2	210°C
Tenax-GC	400°C

The temperatures at which they begin to show a weight loss from thermal decomposition in air are as follows:

Chromosorb 102	250°C
XAD-2	260°C
Tenax-GC	450°C

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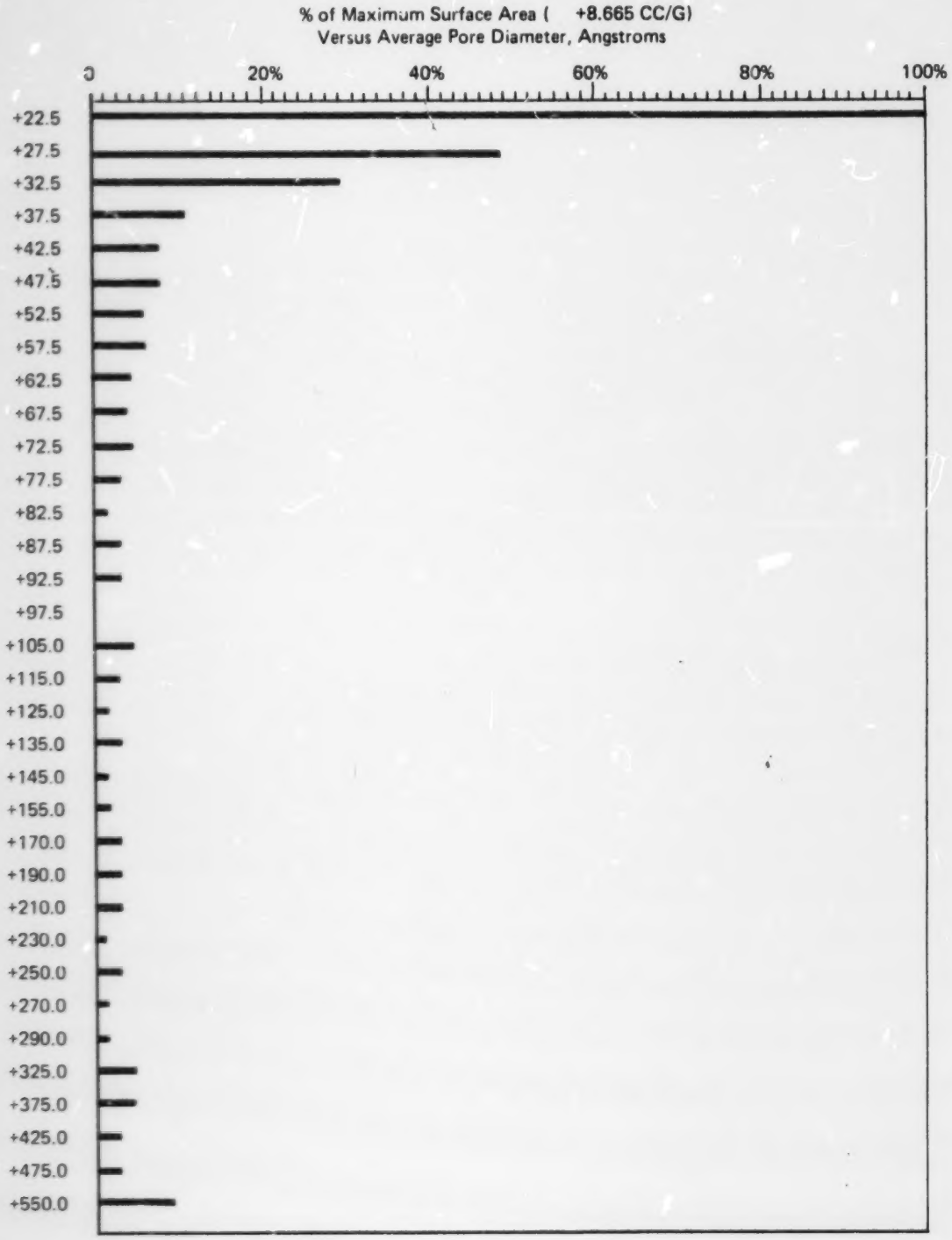


FIGURE 1 INCREMENTAL SURFACE AREA DISTRIBUTION (DESORPTION): TENAX GC

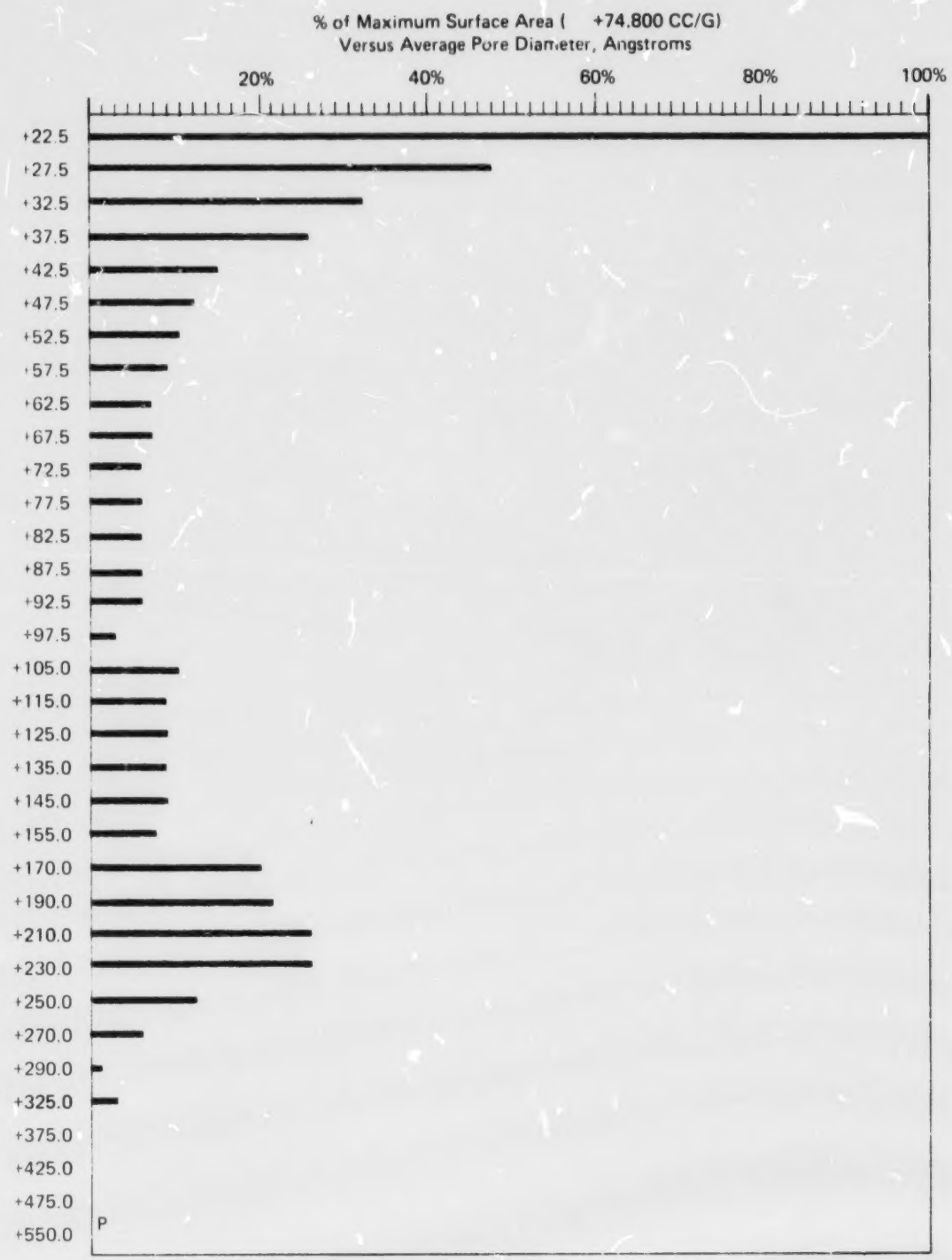


FIGURE 2 INCREMENTAL SURFACE AREA DISTRIBUTION (DESORPTION): CHROMOSORB 102

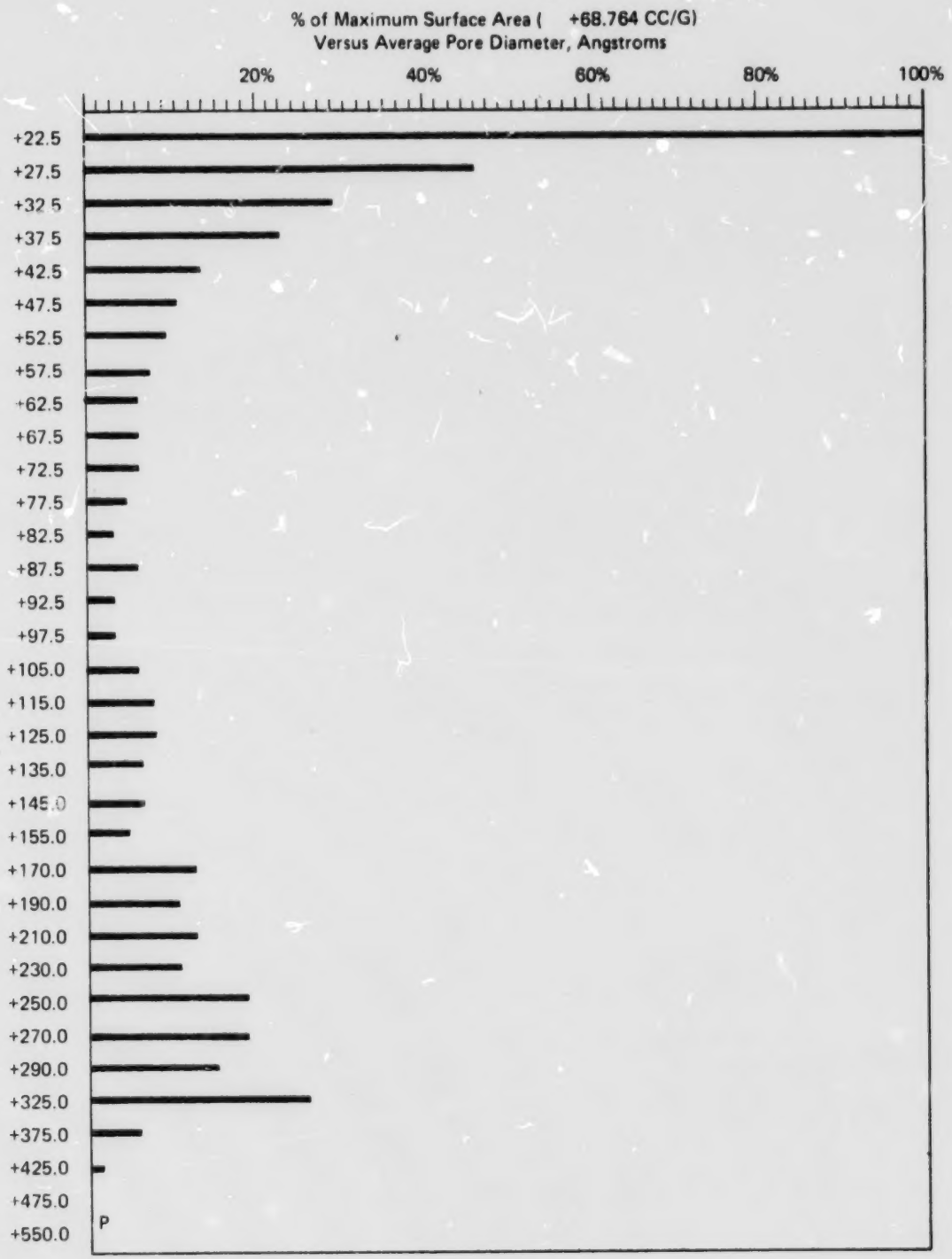


FIGURE 3 INCREMENTAL SURFACE AREA DISTRIBUTION (DESORPTION): XAD–2

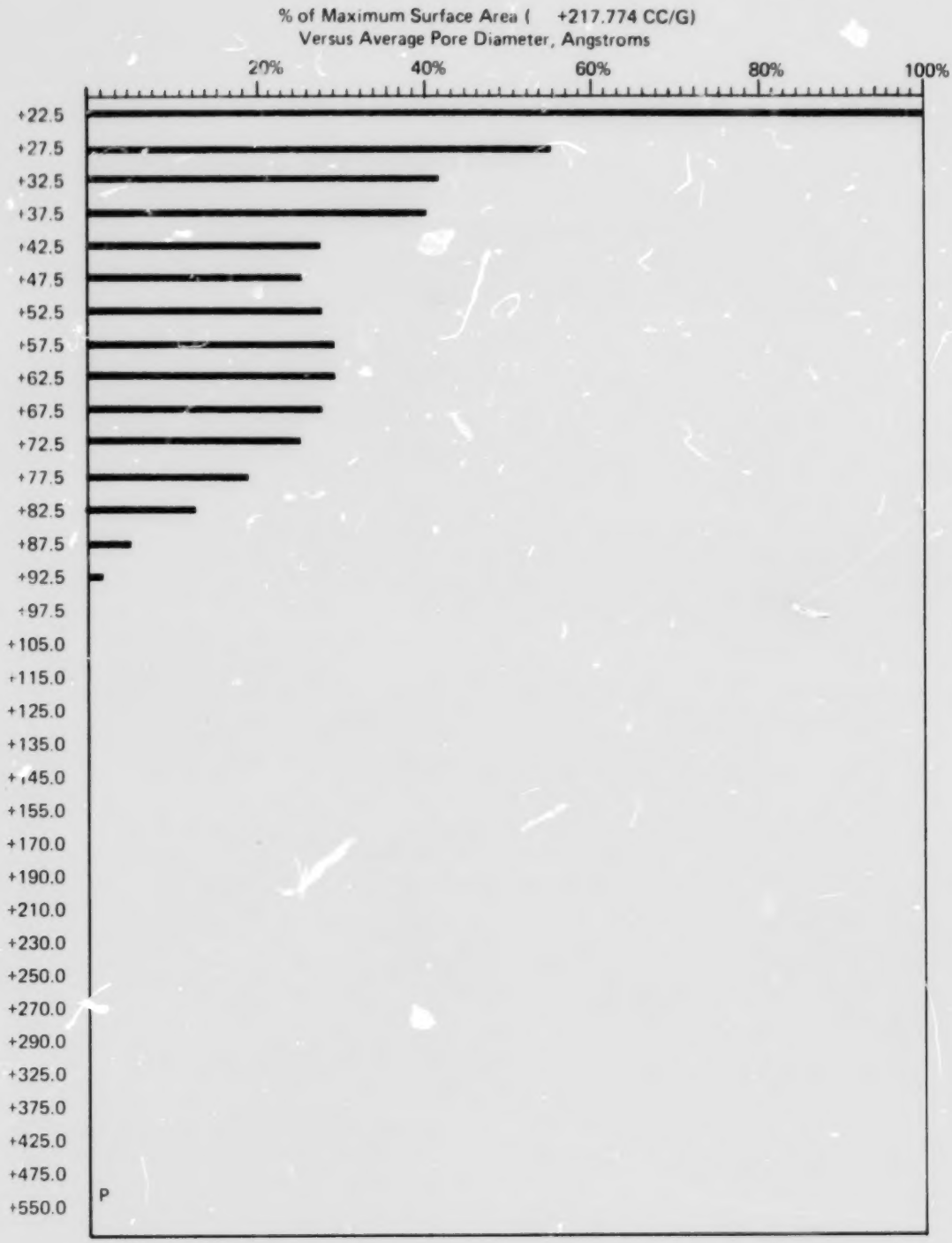
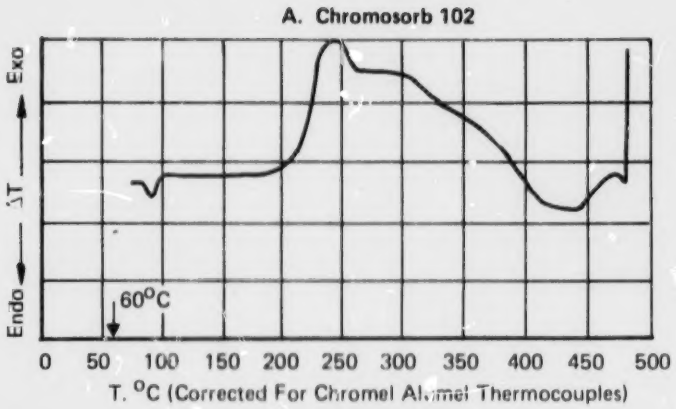
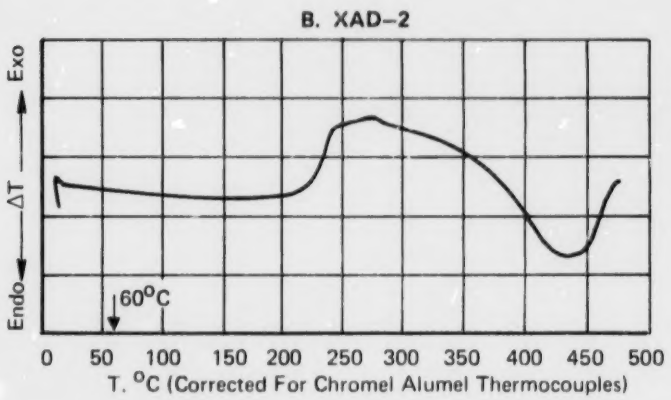


FIGURE 4 INCREMENTAL SURFACE AREA DISTRIBUTION (DESORPTION): XAD–4





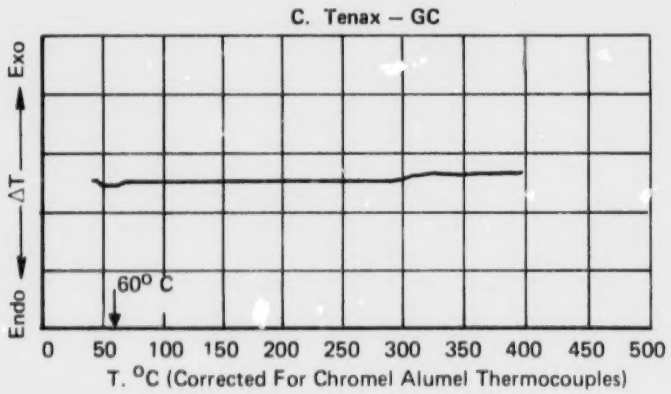
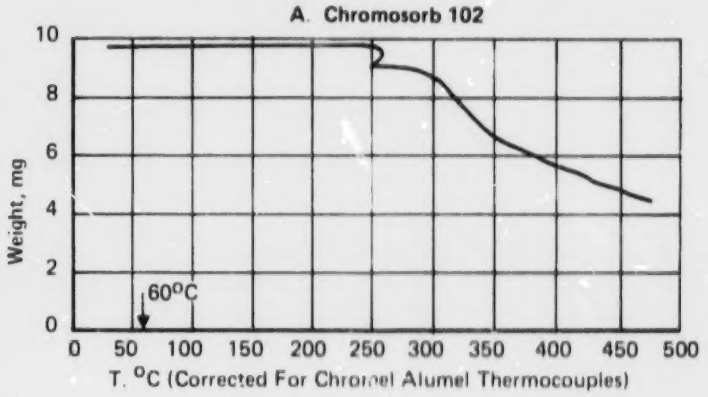
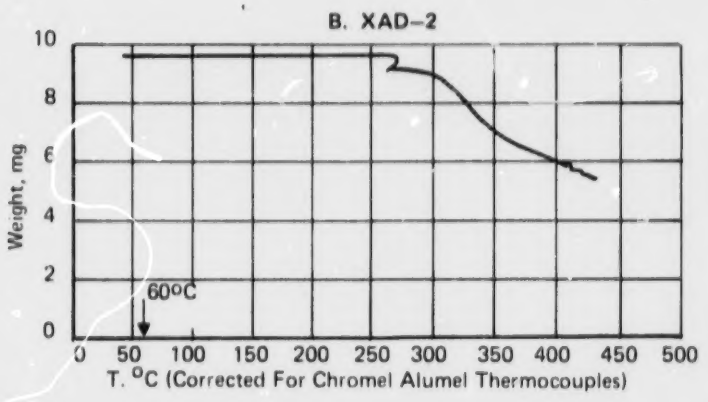


FIGURE 5 DIFFERENTIAL SCANNING CALORIMETRY DATA





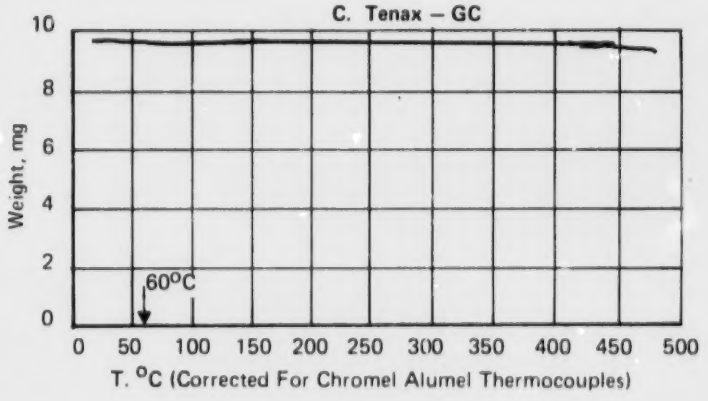


FIGURE 6 THERMOGRAVIMETRIC ANALYSIS DATA

Thus, while Tenax-GC clearly has superior thermal stability, each of the resins appears capable of meeting the 60°C requirement of the SASS train.

Each of the purchased resins considered must be cleaned up before use in sampling trains. The cost of this procedure has been estimated so that a true cost of ready-to-use resin can be used for comparison. At ADL, about 1000 cc of resin is cleaned at a time in giant Soxhlet extractors. After cleanup the resin must be dried. It is estimated that about 4 labor hours (A cost of $30 per hour has been used for estimating purposes) are required for Tenax-GC extraction and 4 for drying, packing, etc. Thus, 1000 cc of Tenax-GC (140 g) costs about $448 for purchase, $240 for preparation, for a total of $688/140 g or about $500/100 g (714 cc). XAD-2 cleanup is more extensive and takes about 8 labor hours for cleanup and 4 for drying. Thus, 1000 cc of XAD-2 (380 g) costs about $3.34 for purchase, $360 for preparation, for a total of $363/380 g or about $100/100 g (263 cc).

In the SASS train, a 7 cm dia x 9 cm deep sorbent trap will hold 343 cc. Therefore, a cost/trap for XAD-2 and Tenax-GC would be about $130 and $240 respectively. The resins should be reusable in each case, and the recycle cleanup costs are expected to be the same for both.

D. Collection Efficiency Studies

ADL has a joint EPA program with TRW[4] to evaluate efficiencies of incinerators in destroying industrial waste. For that program, Chromosorb 102, XAD-2 and -4 and Tenax-GC were evaluated for their potential use in the sorbent trap section of a modified Method 5 train. Trap geometry, sorbent particle size and quantity were studied to find an optimum for the train. The final trap had to have a minimum pressure drop, good initial collection efficiency and good capacity for pollutants.

Initial studies were done using diesel exhaust as a challenge. Diesel exhaust is hot (120 - 150°C), wet, and contains a reasonable level of test pollutant. These tests were conducted by running the hot exhaust into a trap held at ambient temperatures with no provision for heating or cooling. Final studies at lower challenge levels were done with dilute mixtures of hexane and decane.

The studies were run as breakthrough experiments. The pollutants were initially measured at the entrance to the trap to determine the challenge level, and the exit from the trap was then continuously monitored with a hydrocarbon analyzer. Before discussing the data obtained, it is useful to define some terms in describing collection efficiency and breakthrough (or capacity). Figure 7 shows an idealized sorbent bed test experiment. A typical sorbent trap will not collect with 100.00% efficiency and thus there will be a finite initial exit concentration. When the bed has begun to reach its capacity, the pollutants will start to break through.

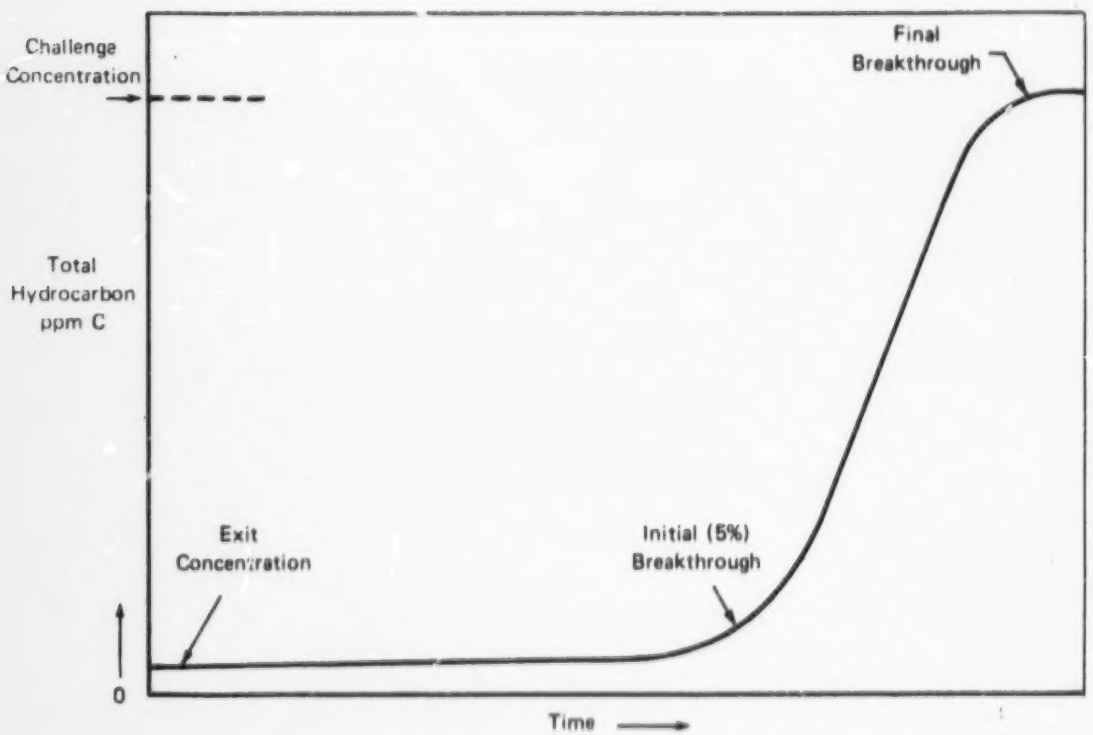


FIGURE 7 SORBENT TRAP BREAKTHROUGH EXPERIMENT

The point at which these pollutants equal 5% of the challenge concentration is frequently taken as the bed capacity for analytical purposes. Final 100% breakthrough occurs sometime later.

The data obtained in the screening experiments is given in Table 2. Sample was pulled through the sorbent traps at 28.3 ℓpm (1.0 cfm) using a standard RAC control module. For these tests, the sorbent was held in a piece of standard pipe. Bed dimensions were about 4.0 cm ID x 7 cm deep in all but one case but were not measured accurately. The sorbent quantity (which was weighed accurately) gives an index of bed depth.

It was never possible to purify XAD-4 acceptably as indicated by GC analysis of washings, and it was thus dismissed as a real candidate. XAD-2 and Chromosorb 102 appear to behave quite similarly in collection efficiency and capacity. Diesel exhaust contains a wide distribution of chemicals, including some very low molecular weight species (methane, formaldehyde, etc.) which are not collected in these traps. The XAD-2 and Chromosorb 102 have an apparent capacity of about 1300 - 300 = 1000 ppm C or 500 mg/cu m for 20 - 25 minutes. This amounts to the collection of 350 mg trapped from the 707 liters collected over the 25-minute period. The same amount seems to be collected on either 20 or 40 grams of XAD-2, so it has a capacity of about 9 mg/g - 18 mg/g (350 µg/40 g - 350 µg/80 g) of sorbent for diesel components.

None of the sorbents of interest has any useful capacity for hexane, an observation reported by others and observed in the previous diesel exhaust studies. The best comparison to Tenax-GC and XAD-2 comes from the decane experiments. XAD-2 in two runs showed no breakthrough after three hours of a 180 ppm C challenge. The Tenax-GC trap broke through after 5 - 10 minutes.

Based on these experiments, it was felt that XAD-2 represented the best general choice of sorbent for use in a wide variety of tests.

Particle size did show measurable differences in the trap pressure drop, but these differences are minor for the most part, except for Chromosorb 102, whose pressure drop was too high for reliable train operation.

To further test the thermal stability of XAD-2 resin for trace organic analysis, two blank experiments were run. Laboratory air was heated to 100°C and 120°C and pulled through 40 g beds of XAD-2, held at those same temperatures for three hours at 28 ℓpm (1 cfm). The sorbent traps were extracted overnight with pentane in the continuous extractor, the extracts concentrated to 0.2 mℓ and aliquots analyzed by GC/FID. No species could be observed in the chromatograms, except for a minor solvent impurity.

TABLE 2

Sorbent Trap Breakthrough Experiments

[All experiments run at 28.3 lpm (1 cfm) flow rate]

Run	Resin[a]	Amount[b] (g)	Size (Mesh)	ΔP in. Hg.	Source[c]	Total Run Time (min)	Hydrocarbon Levels (ppm C) Inlet Challenge	Exit Initial	Exit 1 Hr.	Exit Final	5% Break Time (min)
1	C102	20	48-60	5.6- 7.4	Diesel	55	1300	265	-	470	20
2	C102	20	60-80	5.7-11.1	Diesel	70	1250	210	180	180	None
3	X2	20	20-50	3.5	Diesel	60	1300	320	800	800	20
4	X2	40	20-50	2.1- 3.0	Diesel	135	1350	270	390	790	25
5	X2	40	30-50	4.0- 4.5	Diesel	133	1200	210	320	640	25
6	X2	40	30-40	2.5	Diesel	80	1300	260	360	340	25
7	C102	22	48-60	4.0	C6	40	160	60	-	120	0-5
8	X2	37	30-40	2.3	C6	40	140	4	-	82	5-10
9	X4	33	20-50	2.6	C6	70	180	6	42	70	20
10	T	12	35-60	3.5	C6	20	160	115	-	160	0-5
11	T	11	35-60	3.1	C6	5	160	19	-	103	0-5
12	X2	34	20-50	2.5- 2.8	C10	180	140	4	-	-	None
13	X2	30	30-50	2.7- 2.8	C10	180	140	4	2	2	None
14	T	11	35-60	3.6	C10	55	200	6	-	88	5-10

a C102 = Chromosorb 102, X2 = XAD-2, X4 = XAD-4, T = Tenax GC

b Bed dimensions for all were about 4.0 cm ID x 7 cm deep, except run 3 was 4 cm deep

c Diesel = diesel exhaust, C6 = hexane in air, C10 = decane in air

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E. Evaluation of Other Literature References

A number of papers have been published in the last few years dealing with methods for sampling and analysis of organic pollutants. The novel methods involving the macroreticular resins have used both the styrene (Chromosorb, XAD) and phenyl ether (Tenax-GC) type materials. Unfortunately, very few papers have dealt with the comparative performance of each type of resin. Many of the papers have dealt with research approaches using thermal desorption for GC analysis, and for these studies Tenax-GC clearly has been a choice material. A more general examination of these papers, however, shows that several resins work quite well for the approach being considered in the SASS train.

The paper by Pellizari[9] demonstrates comparable efficiency of the Chromosorbs and Tenax-GC. The Chromosorb 101 used in that study has only 25 m^2/g. Pellizari[10] also found similar results in quantitative thermal desorption from Chromosorb 101 and Tenax-GC. (see page 559 of article)

Russell[11] has also shown similar behavior in the comparative performance of the Poropak series polymers (equivalent to the Chromosorbs) and Tenax-GC.

Junk,[12] et al have published results in the recovery of trace organics from water at the ppm-ppb level using XAD-2 resin.

F. Conclusions and Recommendations

Based upon the information available in April 1976, XAD-2 and Tenax-GC appeared to be suitable resins to consider using in the sorbent trap of the SASS train for some applications. The pressure drop in an XAD-2 bed is less than the Tenax-GC, and the final use cost of XAD-2 is about one-half of that for Tenax-GC. For general use, XAD-2 appears to have much greater capacity than Tenax-GC. XAD-2 is readily available in large quantities.

The use of XAD-2 was recommended for the sorbent module of the SASS train. Further studies were recommended to describe the quantitative behavior of the resins under sampling conditions.

New data should include information on collection efficiency (at SASS velocities), capacity and recovery. Tests should be done at trace levels in streams which realistically simulate process streams.

III. EVALUATION PROGRAM

A. Approach

As discussed in the introduction, two basically different approaches have been taken to the collection of data for this program. One involves the straightforward method of collecting pollutants from a gas stream using the critical components of a sampling train. The other uses a gas chromatographic method. The first method is time-consuming and difficult to use with hazardous compounds, especially Agent Orange and TCDD but is necessary to verify the correlation with the second method. The GC method allows a more rapid screening, enables one to work with hazardous compounds in a safer laboratory experiment, and potentially allows the evolution of a general correlation between collection efficiency and compound volatility.

To properly use sorbent traps for the collection of organic vapors in sampling trains, such as the SASS train, it is necessary to characterize the resins used in the traps for their initial collection efficiency and their capacity for the compounds being collected. These factors are affected by the concentration of the organic vapors in the stream being sampled and by the vapor pressures of the specific compounds.

Collection efficiency is defined in the conventional manner as

$$\frac{\text{(Inlet-Outlet) concentration}}{\text{Inlet concentration}} \times 100$$

for most resins, with enough effectiveness to be of interest, the initial collection efficiency is almost always 98 - 100%. In the course of sampling, a sorbent trap will lose its efficiency by exceeding the capacity of the trap. This may happen in two ways.

For streams with a high concentration of organic vapors, the pores of the resin will become filled and the trap will, in essence, overflow. This phenomenon may be thought of as a weight capacity. For low organic vapor concentration streams the capacity, or holding power, of the trap is exceeded by virtue of the species being stripped out of the trap by the air being sampled, as in a gas chromatography experiment. This capacity breakthrough phenomenon is a volumetric (gas) capacity (Vg).

The retention volume (Vg) obtained from the GC type elution analysis is equivalent to the same value obtained from a frontal analysis experiment where one uses a steady state challenge concentration. This similarity has been used by many researchers to study the fundamental properties of chromatography and is discussed in several references including those by Purnell[21,22] and Hildebrand.[23]

It has been shown[13] that the retention time of a chemical on a sorbent is directly proportional to the equilibrium adsorption capacity of the sorbent. Other studies[14] have shown that retention times are a regular function of a homologous series of compounds giving linear relationships with such simple parameters as carbon number.

Based upon the results of these previous studies and the results presented in the Background (Section II), both the GC and sampling train experiments were conducted with a series of n-hydrocarbons in order to determine the basic vapor pressure (boiling point) relationship with trap capacity and breakthrough. A wider range of compound types were studied in the GC experiments, including examples of the pollutants of direct interest for the shipboard incineration studies.

B. Experimental

1. Chromatographic Apparatus

Special stainless steel columns were constructed to hold the resins for mounting in a conventional gas chromatograph. The dimensions to be used were arbitrary, but a minimum of resin was used in order to keep the retention times short. Since the SASS sorbent trap was 9 cm deep (it is now 7 cm deep), a 9-cm column was constructed from 1/4 in (0.635 cm) O.D. tubing of 0.020 in (0.51 mm) wall thickness. The column was terminated by a dead volume 1/4 x 1/16 in Swagelok fitting containing a 2-μm stainless steel frit to hold the resin in place. The column was connected to the injector and detector by use of short lengths of 1/16 in stainless steel tubing. The volume of the column was 2.50 mℓ. The column weight was determined before and after each time it had been packed with either XAD-2 or Tenax-GC so that the weight of resin was accurately known for each experiment.

A Varian 2100 GC was used equipped with a flame ionization detector. Helium carrier gas was used and maintained at a flow rate determined to be 1.12 mℓ/sec. This rate gives about one-tenth of the linear velocity obtained in a SASS trap. Higher gas flows extinguished the flame.

Solutions were prepared in carbon disulfide solvent and injected in the normal way. The time for the compound being studied to reach its maximum in the elution profile was recorded as the value of interest. This point of peak maximum corresponds with the 50% breakthrough point for a continuous flow stream containing a low concentration of the pollutant. A set of typical elution curves obtained for octane (C_8) and phenol on XAD-2 are shown in Figure 8.

The volumetric capacity (Vg) in mℓ/g was calculated from the elution time data, flow rate and resin quantity as

FIGURE 8 GC ELUTION PROFILES ON XAD–2

where tr = retention time in seconds to peak maxima

F = carrier gas flow rate in mℓ/sec corrected to STP 273°C, 760 mm Hg)

g = resin (XAD-2 or Tenax-GC) weight

It is necessary to conduct the volumetric capacity studies in a range where the elution time is independent of sample size. To experimentally determine this point, a series of injections of octane of varying quantity either neat or in carbon disulfide, were made on both the XAD-2 and Tenax-GC columns. The variation of retention time observed for XAD-2 is shown in Figure 9. Any quantity below 0.01 µℓ of octane gave identical times. For Tenax-GC, the corresponding value was about 0.003 µℓ. For all of the subsequent studies, 1 µℓ of a 0.1% solution of the compound in carbon disulfide solution was injected, or 0.001 µℓ of compound.

An arbitrary cut-off time of 4 hours was chosen for termination of any particular experiment, except in a few cases where observations were carried out up to 20 hours. Preliminary experiments indicated that the 4 hour time at 135°C was a factor of 5 - 10 times longer than needed to correspond to the SASS train sampling at 60°C for 4 hours.

2. Steady State Concentration Apparatus

The experiments designed to test the weight loading capacity of the sorbent resins involved the continuous sampling of air containing a known concentration of chemical through sorbent traps and measuring the trap breakthrough. The equipment used for these experiments is shown schematically in Figure 10.

Hydrocarbon and particulate free air was fed to the sampling system at about 100 ℓpm. A branch in the air line allowed water to be added so that the effect of moisture in the air could be studied. Test levels of about 12 - 20% RH were generated. The water was vaporized with the tube furnace.

A precalibrated syringe drive allowed the addition of controlled amounts of hydrocarbons to the air stream. Test concentrations ranging from 10 mg/cu m to 1000 mg/cu m were generated.

The XAD-2 and Tenax-GC sorbent resin was held in glass sorbent traps which had previously been designed for and used on an RAC Method 5 type train. The trap, shown schematically in Figure 11, contained a volume of approximately 100 mℓ of resin. Sampling was maintained at 28 ℓpm (1 cfm) using the control module of the RAC Staksampler.

Breakthrough was determined by monitoring the air concentration levels using a heated Beckman 402 flame ionization hydrocarbon analyzer. After a steady state concentration of hydrocarbon had been achieved in the delivery line, as determined by the HC analyzer, the HC analyzer was switched to the trap exit and sampling through the trap initiated.

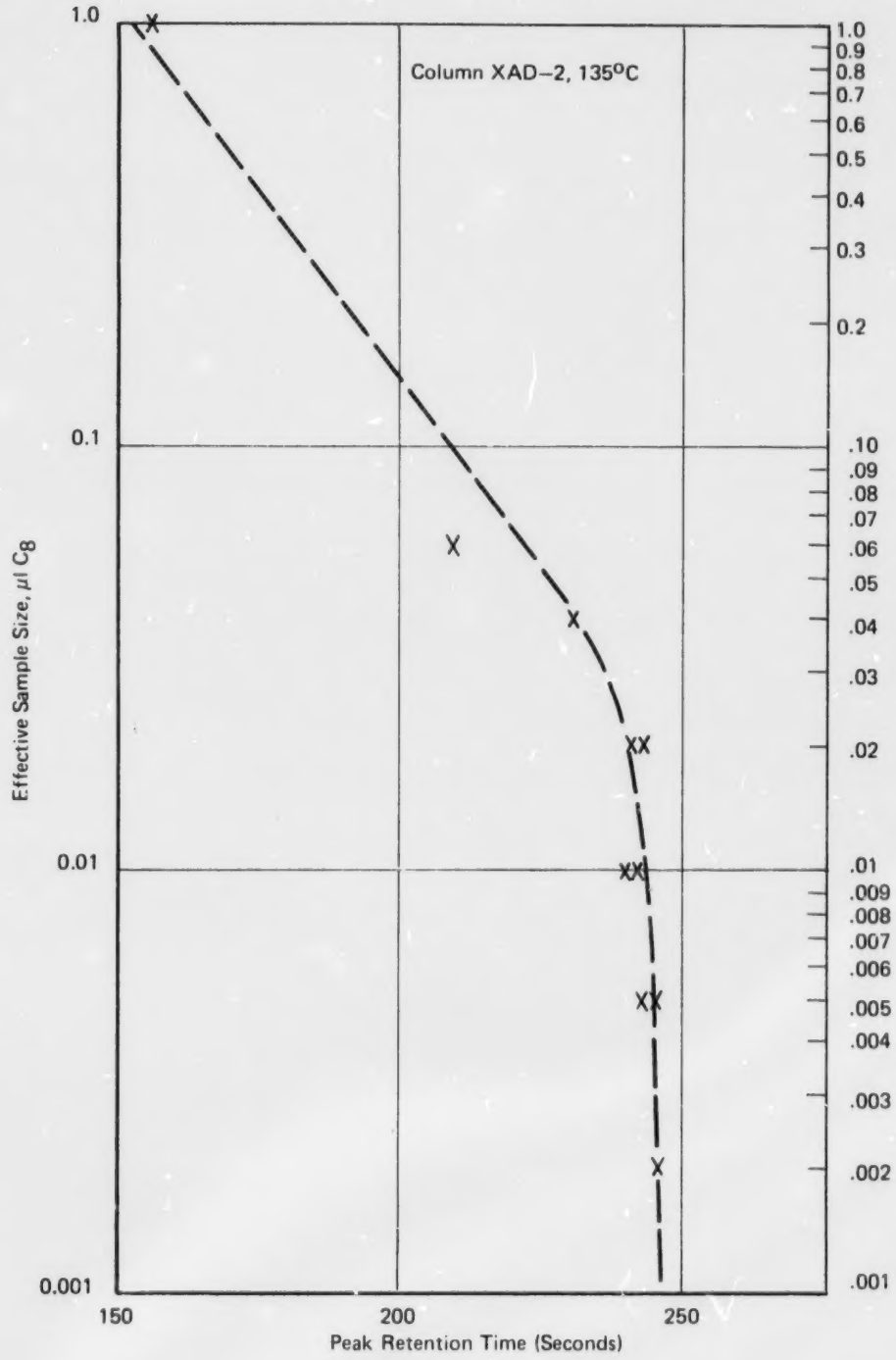

FIGURE 9 VARIATION OF PEAK ELUTION TIME WITH SAMPLE SIZE

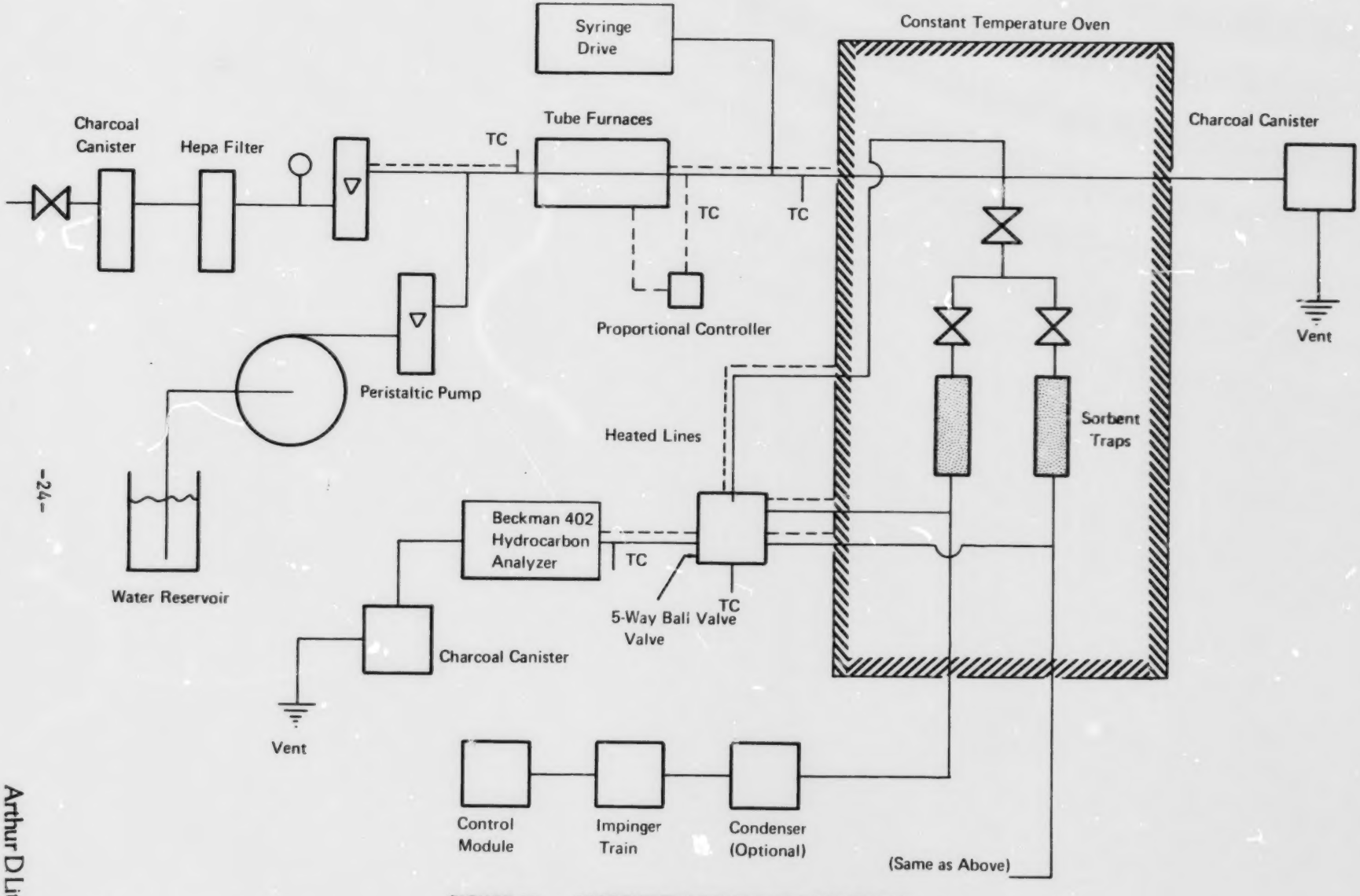

FIGURE 10 SORBENT TRAP EXPOSURE APPARATUS

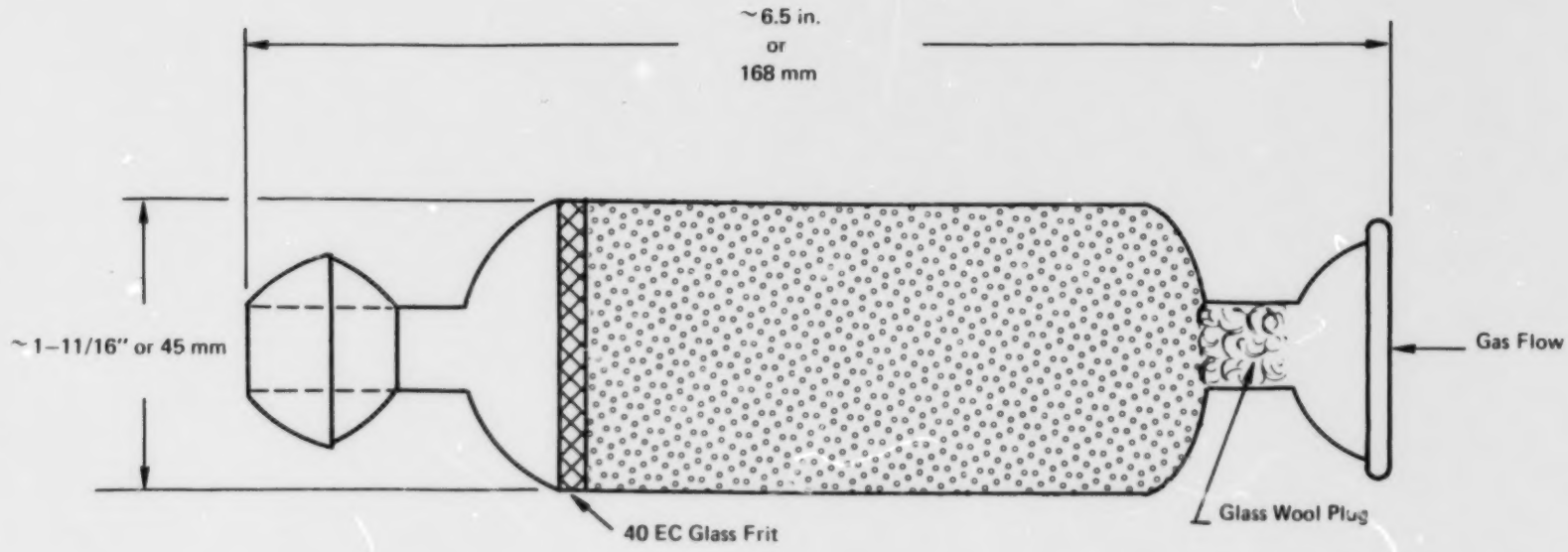

FIGURE 11 SORBENT TRAPS

Although the system was designed for the study of two traps simultaneously, we found that it was only possible to keep track of one trap at a time. Sampling was continued either until the trap had reached 100% breakthrough or for four hours, whichever came first. A typical curve obtained from the data for a 100 mg/cu m challenge of n-decane on Tenax-GC is shown in Figure 12.

A 4-hour sampling period with these traps is about equivalent to the same time period with the SASS trap. Although the SASS train samples at 5 cfm (vs 1 cfm here), the SASS train sorbent trap contains 4.5 times as much resin.

For these experiments, the sorbent trap was maintained at 60°C, the original SASS train sorbent trap design temperature. (As indicated earlier, the sorbent trap operating temperature has been lowered to 20°C.)

C. Results of GC Experiments, Vg's

Experimental data have been obtained on a number of compounds. The compounds were chosen partly to represent a smooth homologous series for examination of vapor pressure relationships and partly to reflect those compounds of direct interest to the incineration studies.

Compounds studied extensively were:

Compound	Molecular Formula	Text Code
n-Hexane	C_6H_{14}	C_6
n-Octane	C_8H_{18}	C_8
n-Decane	$C_{10}H_{22}$	C_{10}
n-Dodecane	$C_{12}H_{26}$	C_{12}
n-Tridecane	$C_{13}H_{28}$	C_{13}
Benzene	C_6H_6	C_6H_6
Naphthalene	$C_{10}H_8$	$C_{10}H_8$
Dichlorobenzene	$C_6H_4Cl_2$	$C_6H_4Cl_2$
Phenol	C_6H_5OH	C_6H_5OH
Aniline	$C_6H_5NH_2$	$C_6H_5NH_2$
Limited data were obtained on:		
Agent Orange	2,4-D + 2,4,5-T	AO
Aroclor 1242	--	--
Pyrene	$C_{16}H_{10}$	--
Vinyl chloride monomer	C_2H_3Cl	VCM

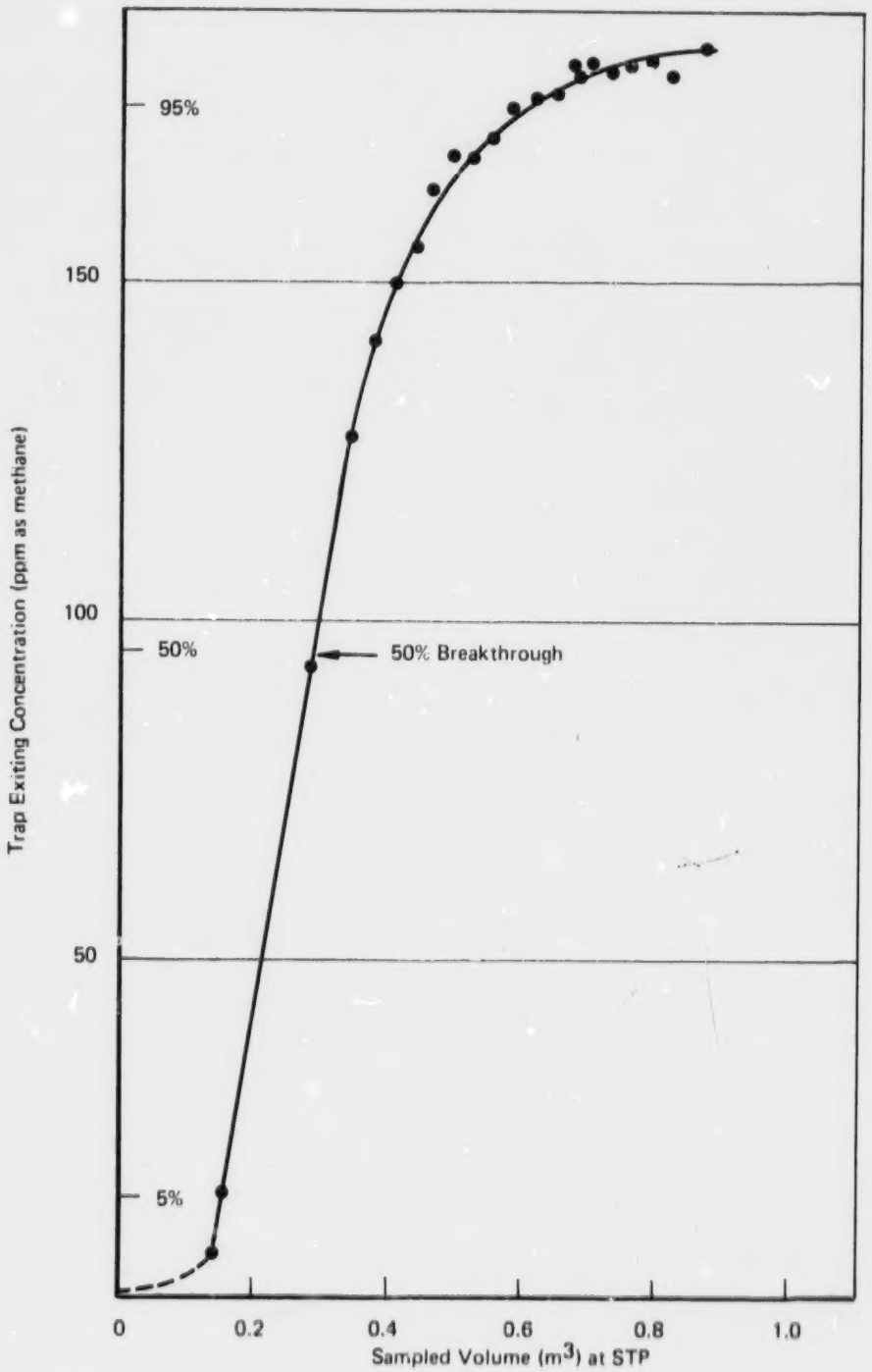

FIGURE 12 **BREAKTHROUGH OF TENAX GC CHALLENGED WITH n–DECANE IN DRY AIR STREAM AT 60°C**

The paraffins were chosen for the systematic vapor pressure relationship study. Benzene, naphthalene and pyrene represent a start into the POM's. Dichlorobenzene and Aroclor 1242 represent the PCB's. Phenol and aniline were chosen to examine compound polarity effects. Agent Orange and vinyl chloride monomer are species to be burned in incinerator tests.

For the first set of compounds, the GC Vg determination tests were each run as a set of four replicates. A fresh column was packed for each set of determinations. The data from the individual experiments are given in Appendix A. Thus, the data obtained represent a reliable estimate of Vg and provide a measure of the variability which can be expected. The specific retention volume data are summarized for XAD-2 and Tenax-GC in Tables 3 and 4, respectively. On the average, the Vg data have about a 10% relative standard deviation.

Experiments were run at 135° and 96°C in order to allow an extrapolation to the SASS train operating temperature of 60°C using the conventional Arrhenius relationship

$$Vg = ae^{-Ea/RT}, \quad \log Vg = a' - \frac{E_a}{RT}$$

Direct observation at 60°C took too long for most of these compounds, but it was possible to obtain data at 60°C, 96°C and 135°C for hexane and benzene. These data are given in Table 5.

The data from Tables 3 - 5 are plotted in Figures 13 and 14 for XAD-2 and Tenax-GC, respectively. Most of the compounds on these plots only have two points to establish the extrapolation to 60°C. To demonstrate the validity of this approach, the data from replicate points for benzene and hexane on XAD-2 in Table 3 were used to establish the lines for these compounds. The additional data given in Table 5 were then plotted on Figure 13 after the lines had been plotted. These data demonstrate the linear relationships between Vg and reciprocal temperature.

For XAD-2 (Figure 13) most of the compound types show similar heats of adsorption (slope). The low molecular weight benzene and hexane show a higher heat of adsorption (smaller slope) which may have to do with their size and diffusion into the smaller pores of the resin. A range of heats of adsorption seem apparent for Tenax-GC (Figure 14). As for XAD-2, benzene shows the highest heat of adsorption. The paraffins (C_8, C_{10}) show the lowest heat of adsorption, while the polar and aromatic compounds show an intermediate heat of adsorption. These heats of adsorption differences between compounds of different polarity might have been expected for the medium polarity Tenax-GC, a polyphenylether. However, one might also have expected comparable heats of adsorption differences between polar and nonpolar compounds on the low polarity XAD-2, a cross-linked polystyrene. The fact that many compounds exhibit

Table 3

Specific Retention Volumes (Vg) for XAD-2
(average of replicates)

Compound	BP(°C)	96°C			135°C		
		Vg	Std dev.	$\log_{10}$ Vg	Vg	Std. dev.	$\log_{10}$ Vg
Hexane, C_6	69	252	54	2.40	43	6	1.63
Benzene, C_6H_6	80	273	42	2.44	49	5	1.69
Octane, C_8	126	2930	335	3.47	271	33	2.43
Decane, C_{10}	174	--	--	--	1840	200	3.26
Phenol, C_6H_5OH	182	4990	645	3.70	477	53	2.68
Aniline, $C_6H_5NH_2$	184	5460	565	3.74	566	72	2.75
Dichlorobenzene, $C_6H_4Cl_2$	180	9850*	--	3.99	924	108	2.96
Naphthalene, $C_{10}H_8$	218	--	--	--	3860	467	3.59

*single value

Vg = specific retention volume of carrier gas in units of mℓ/g of resin.

Average weight of XAD-2 per column was 0.734 ± 0.017 g.

Table 4

Specific Retention Volumes (Vg) for Tenax-GC
(average of replicates)

Compound	BP(°C)	96°C Vg	96°C Std. dev.	96°C $\log_{10}$ Vg	135°C Vg	135°C Std. dev.	135°C $\log_{10}$ Vg
Hexane, C_6	69	--	--	--	13	3	1.11
Benzene, C_6H_6	80	156	21	2.19	27	3	1.43
Octane, C_8	126	659	38	2.82	56	8	1.75
Decane, C_{10}	174	6500	329	3.81	308	28	2.49
Dodecane, C_{12}	216	--	--	--	1540	264	3.19
Tridecane, C_{13}	235	--	--	--	3330	600	3.52
Phenol, C_6H_5OH	182	3080	98	3.49	298	15	2.47
Aniline, $C_6H_5NH_2$	184	4380	179	3.64	418	28	2.62
Dichlorobenzene, $C_6H_4Cl_2$	180	6020	134	3.78	498	34	2.70
Naphthalene, $C_{10}H_8$	218	--	--	--	1870	192	3.27

Vg = specific retention volume of carrier gas in mℓ/g of resin
Average weight of Tenax GC per column was 0.321 $\pm$ 0.027 g.

Table 5

Specific Retention Volumes (Vg) of Benzene and Hexane on XAD-2 at Three Different Temperatures

Compound		60°C	96°C	135°C
Hexane, C_6	Vg	2100	211	38
	$\log_{10}$Vg	3.32	2.32	1.58
Benzene, C_6H_6	Vg	2390	255	47
	$\log_{10}$Vg	3.38	2.41	1.67

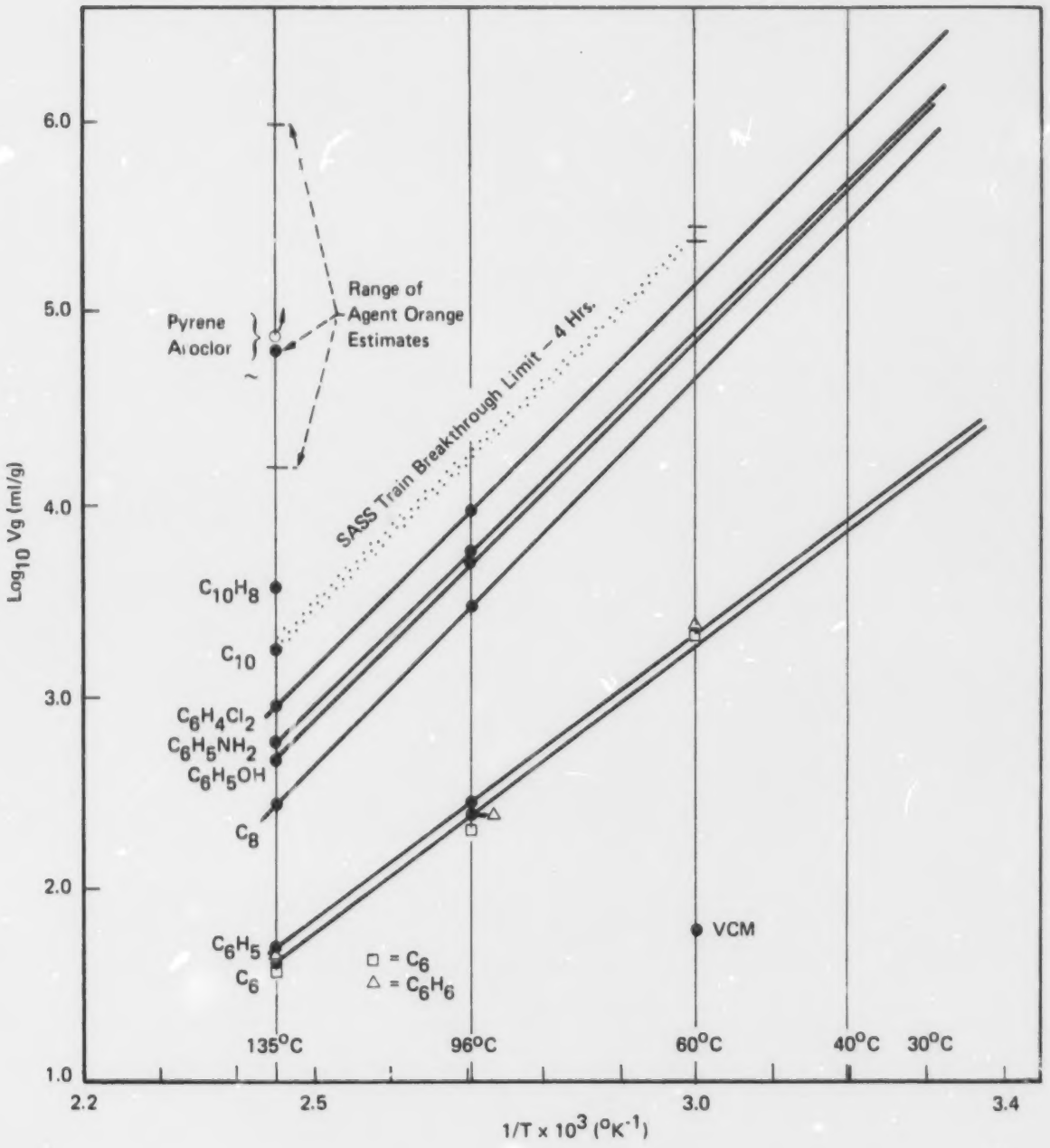

FIGURE 13 TEMPERATURE DEPENDENCE OF SPECIFIC RETENTION VOLUME FOR XAD–2

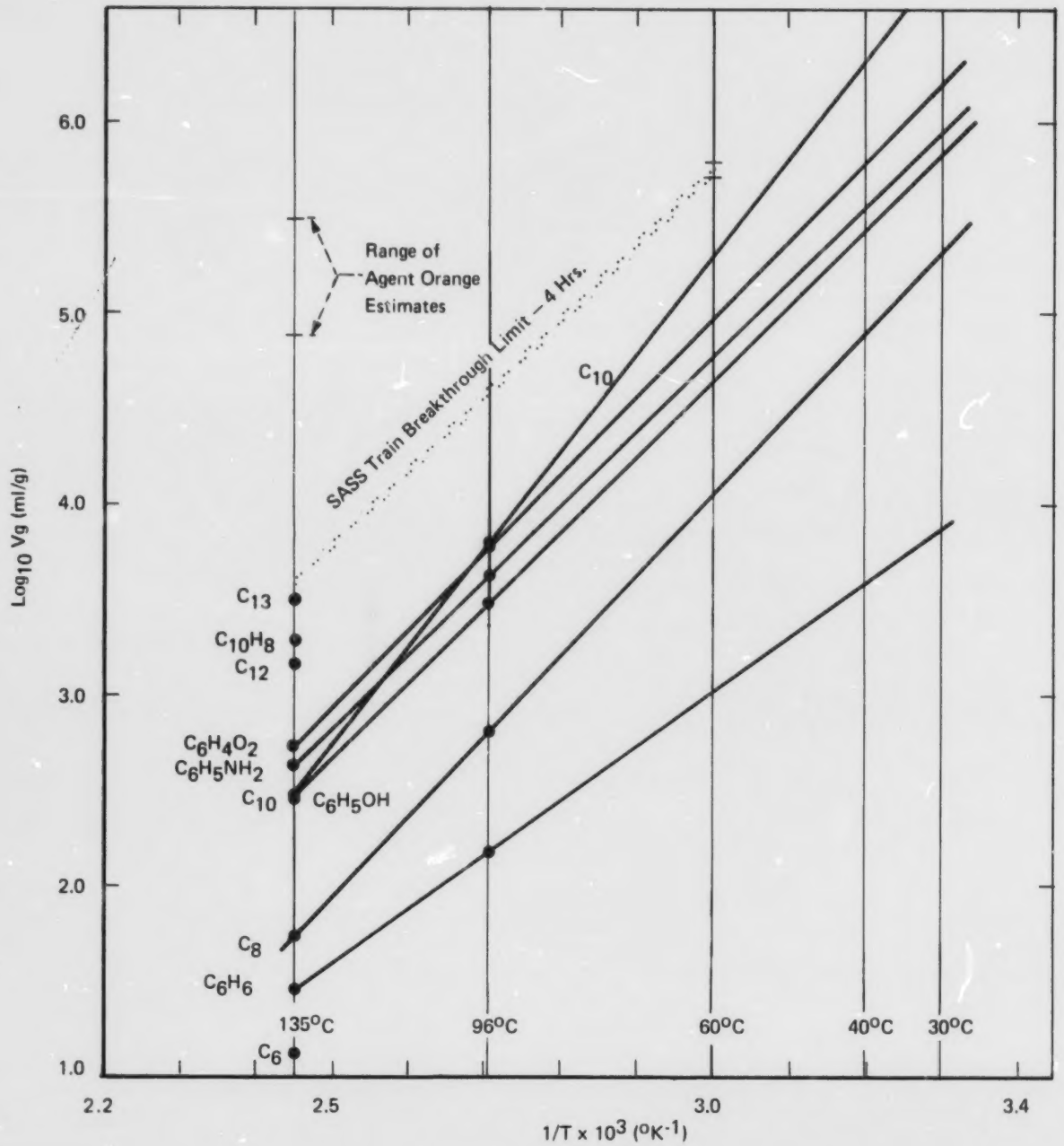

FIGURE 14 TEMPERATURE DEPENDENCE OF SPECIFIC RETENTION VOLUME FOR TENAX GC

the same heats of adsorption dependence on XAD-2 is useful in establishing a Vg-vapor pressure relationship and an elevated temperature screening test.

The Vg data obtained at 135°C on XAD-2 and Tenax-GC are shown plotted against boiling point (vapor pressures at 760 mm Hg) in Figures 15 and 16, respectively. On XAD-2 (Figure 15) a good linear relationship between Vg and boiling point is seen for the n-paraffins. Each of the other compounds falls somewhat below the line established by the paraffins. On Tenax GC (Figure 16), all of the data fall on a smooth curve, and most of it fits on a straight line. However, even though the apparent relationship of Vg to BP is simpler for Tenax GC, the specific retention volumes for each compound are greater on XAD-2 than on Tenax-GC. This is true even for phenol which shows the greatest departure from the paraffin line in Figure 15.

One purpose of examining these Vg-BP relationships was to look for the basis of establishing a simple rapid screening test as a measure of the retention of a given compound based upon limited data. Clearly, more experimental results will have to be obtained before these relationships can be completely defined on a quantitative basis. The basis for such a relationship does indeed exist, as demonstrated by these data and particularly by the results obtained by Kiselev[14] and his co-workers.

Kiselev recently published an extensive series of Vg values obtained on several resins, including Chromosorb 101. Chromosorb 101 is chemically identical to XAD-2 (and Chromosorb 102) and differs primarily in that its surface area is only about 30 m^2/g vs. the 350 m^2/g surface area for XAD-2. That data nicely support the Vg-BP relationship and are based on the study of a large number of compounds and have, therefore, been examined in greater detail for this report.

The Chromosorb 101 data itself from the Kiselev paper are given in Appendix B. The logarithm of relative specific retention volume Vg/VgC_6H_6 (all Vg data were expressed relative to Vg benzene equal to 1.00) vs. boiling point of the compounds have been plotted versus boiling point in Figure 17. An excellent linear relationship with boiling point is observed, encompassing all the data within a single line. The furthest outlier in the data is hydroquinone, which is a very polar compound. A similar relationship is to be expected for XAD-2. We may expect two to four sets of lines for XAD-2 for the grossly different polarity classes of compounds, where the major difference in the sets would be the intercepts of the lines.

The other purpose of establishing the Vg-BP relationships is to enable the prediction of the behavior of compounds for which Vg data are not available. This is especially pertinent for Agent Orange and other compounds which take so long to elute from the resin that it is difficult to determine their Vg value. It also eliminates the need to work with highly toxic compounds such as TCDD.

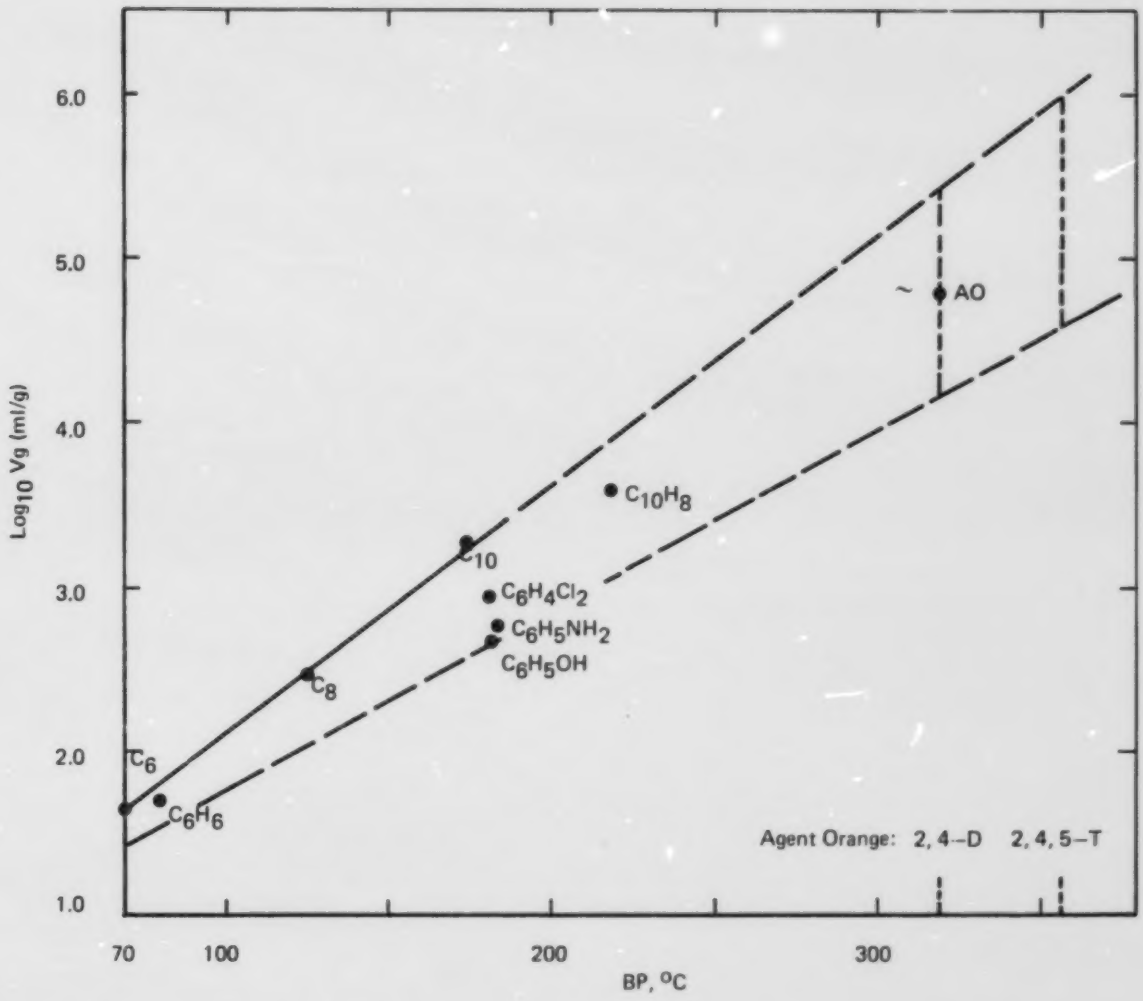

FIGURE 15 RELATIONSHIP OF SPECIFIC RETENTION VOLUME WITH BOILING POINT: XAD–2 Vg DATA AT 135°C

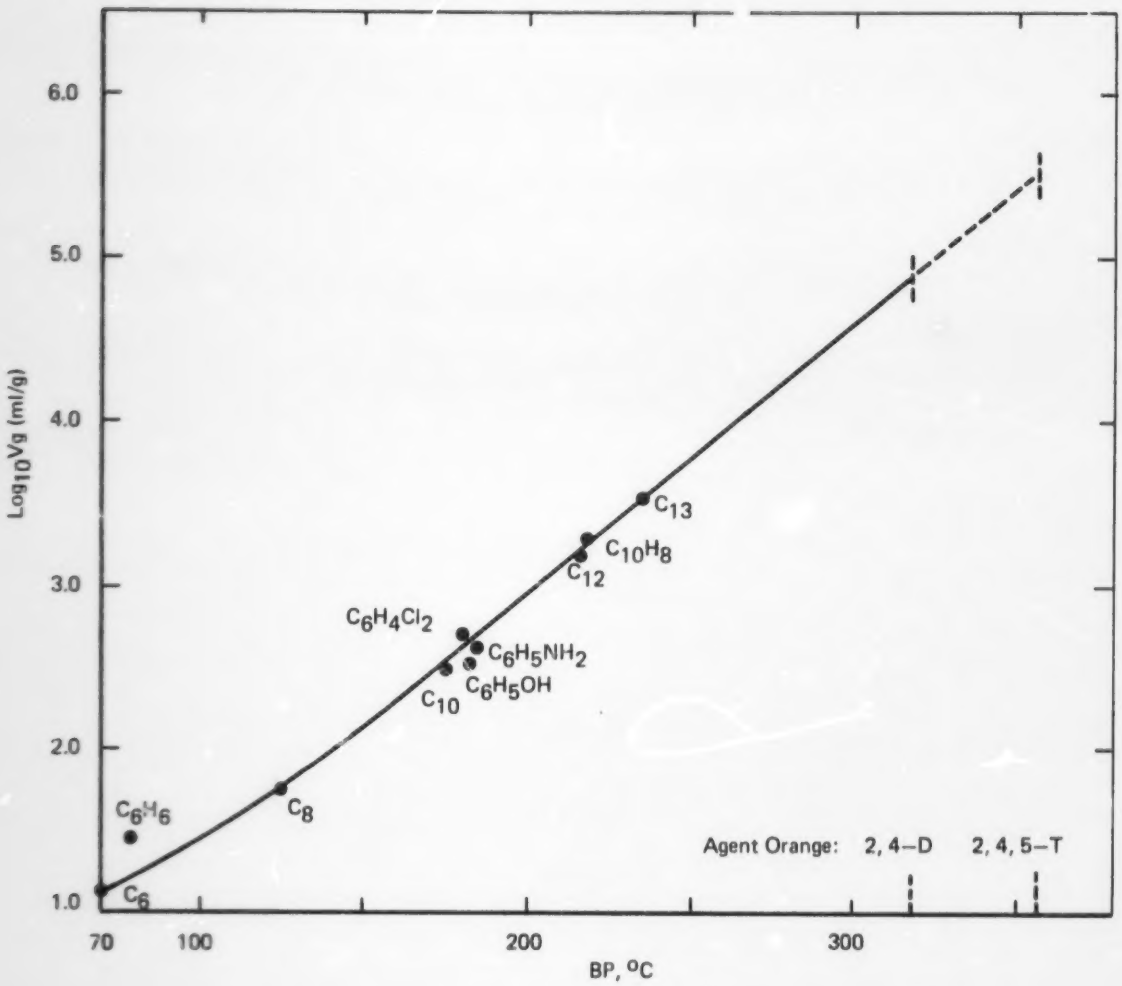

FIGURE 16 **RELATIONSHIP OF SPECIFIC RETENTION VOLUME WITH BOILING POINT: TENAX GC Vg DATA AT 135°C**

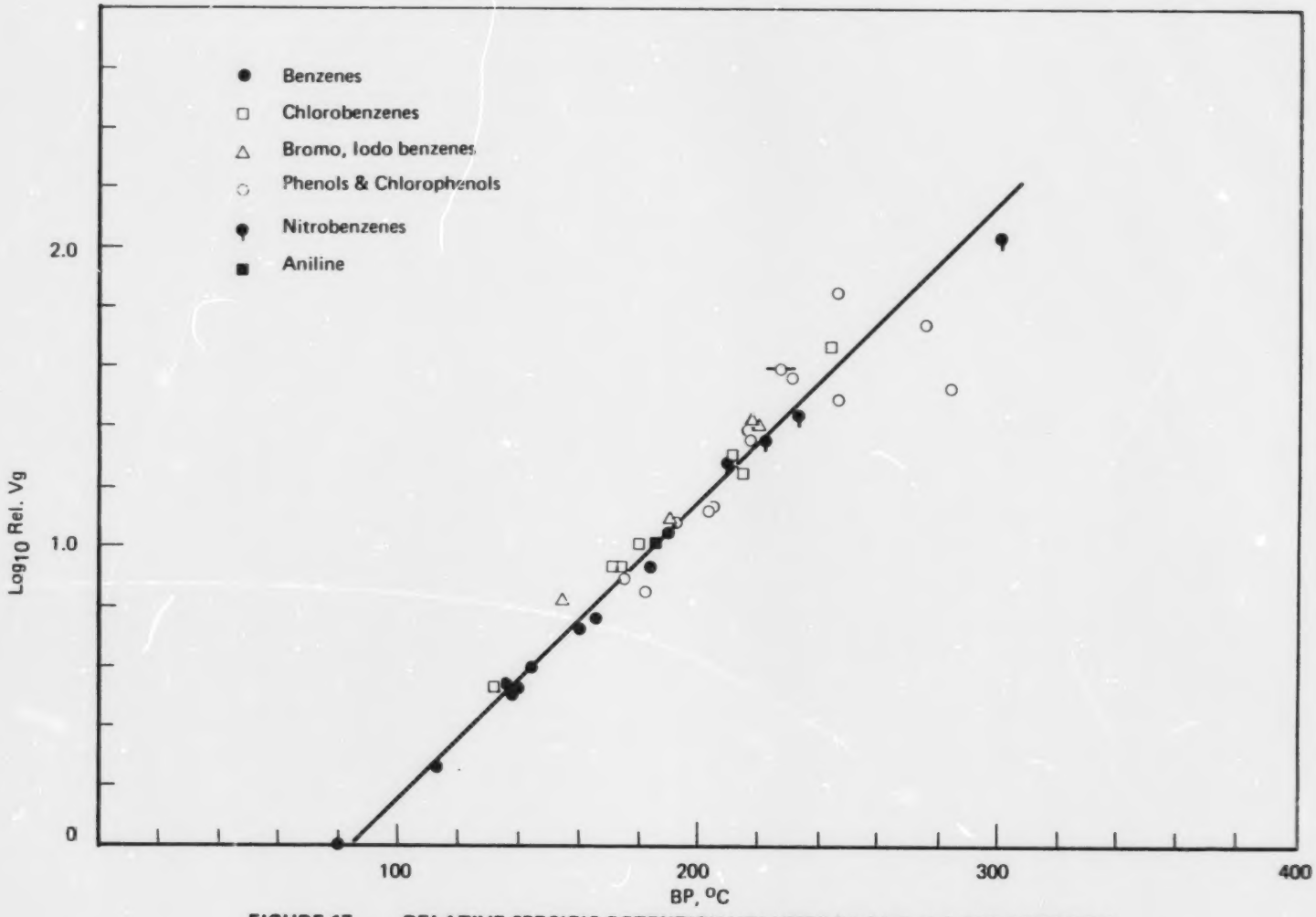

FIGURE 17 RELATIVE SPECIFIC RETENTION VOLUMES ($V_g/V_gC_6H_6$) FOR AROMATIC COMPOUNDS ON CHROMOSORB 101 VS. BOILING POINT. V_g DATA AT 190°C (GVOSDOVICH, KISELEV AND YASHIU)

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In order to extrapolate the relevance of these data to the Agent Orange species, 2,4-D and 2,4,5-T, some additional data were obtained. Using a separate calibrated boiling point GC column and temperature program (per ASTM procedures[15]), the retention times and, therefore, boiling points of 2,4-D and 2,4,5-T were obtained. These values were:

2,4-D (ethylester)	317°C
2,4,5-T (ethylester)	356°C

These points are indicated on the BP axis of Figures 15 and 16. In order to estimate the Vg's for XAD-2, the line for the paraffins (Figure 15) was extended and a second lower limit was estimated and drawn in for polar compounds. The Vg range for the two primary species in Agent Orange can then be estimated from these lines, and similarly for Tenax-GC in Figure 16. The estimates obtained are

	$\log_{10}$Vg (at 135°C) on XAD-2	$\log_{10}$Vg (at 135°C) on Tenax-GC
2,4-D	4.2-5.4	4.9
2,4,5-T	4.6-6.0	5.5

These Vg values are in turn plotted on the Vg - 1/T curves in Figures 13 and 14.

In order to relate these data to retention in the SASS or modified Method 5 train, we must have the comparable Vg data for these trains. Each train holds a certain amount of resin in the sorbent traps and pulls a certain volume of gas in a 1 or 4 hour period. From these data one can calculate the value of Vg (or $\log_{10}$Vg) which a compound must have to be completely retained by the trains. Table 6 contains the relevant data for each sampling train and resin combination. The Vg (Log_{10}Vg) values calculated are lower limits. The compounds must have a Vg equal to or greater than this value (at 60°C) in order to be completely retained by the resin. These Vg limit values for the 4 hour sampling period have been plotted in Figures 13 and 14. Using a slope for these values most similar to the non-paraffins, the limit values can be extrapolated to 135°C. The stippled line generated by this exercise represents the bounds of the SASS train collection efficiency, for low input level challenge concentrations.

For XAD-2, compounds boiling above C_{10} would be completely retained in the SASS train, while those boiling below may be partially or completely lost. For Tenax-GC, the compounds must have a volatility lower than C_{13}. Clearly for both resins, each of the Agent Orange species would be completely retained, in terms of volumetric breakthrough. As discussed later, a compound could always exceed the weight capacity regardless of its Vg if a large enough quantity is collected. The

Table 6

Relationship of SASS and Modified Method 5 Trains
to Specific Retention Volume (Vg) Data

	Sampling Time (Hrs)	Sampling Volume (M^3)	Sorbent Trap Volume (mℓ)	XAD-2 Resin Cap(g)	XAD-2 Breakthrough Vg(mℓ/g)	XAD-2 Breakthrough $\log_{10}$Vg	TENAX-GC Resin Cap(g)	TENAX-GC Breakthrough Vg	TENAX-GC Breakthrough $\log_{10}$Vg
SASS	4	34	445	130	260,000	5.42	57	596,000	5.78
141 ℓpm (5 cfm)	1	8.5			65,000	4.81		149,000	5.17
Modified Method 5	4	6.8	100	29	234,000	5.37	13	523,000	5.72
28.3 ℓpm (1 cfm)	1	1.7			59,000	4.77		130,000	5.12

density XAD-2 = 0.293 g/mℓ
density Tenax-GC = 0.128 g/mℓ

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less volatile TCDD would be retained even longer than the primary Agent Orange species.

In order to conclude this preliminary study, Vg experiments were conducted (Table 7) directly with Agent Orange, POM's (pyrene) and PCB's (Aroclor 1242) on XAD-2 at 135°C. Neither the Aroclor nor pyrene showed breakthrough after about 16 hours. Agent Orange showed an indication of breakthrough corresponding to the reported Vg. This value should be related to the 2,4-D component and the Vg value is shown plotted in Figures 13 and 15. The observed approximate value falls just in the middle of the projected range of Vg's.

Vinyl chloride monomer was studied at 60°C because of its volatility. As expected, vinyl chloride monomer broke through the trap rapidly, and the sorbent trap is not an acceptable means to collect this material.

D. Results of Steady State Challenge Experiment, Weight Capacities

The primary purpose of the steady state challenge experiments was to obtain capacity data in a manner as close as possible to that which would represent the SASS train sorbent trap operating conditions. In addition to volumetric capacity data, these experiments made it possible to obtain weight capacity data from an overloading of the trap.

The data obtained on XAD-2 and Tenax-GC are given in Tables 8 and 9. Experiments were done at a low concentration level, 10 mg/cu m, to obtain the volumetric capacity data and at higher levels for the weight capacity data. Most weight capacity experiments were run at a 100 mg/cu m challenge. However, some additional experiments were run at higher levels of 500 and 1000 mg/cu m either to test the effect of input concentration on capacity or to obtain breakthrough for those compounds (hexadecane) which did not break through at a lower challenge level. The volumetric breakthrough point was taken as the volume when the breakthrough had reached 50% of the input challenge level. The weight capacity was taken at that same point by calculating the amount of hydrocarbon that had been removed from the air stream. The decane experiments on both resins show the transition from a volumetric breakthrough to a capacity breakthrough as one goes from an input level of 10 mg/cu m to 100 mg/cu m.

The data show that Tenax-GC has a low weight capacity and even for the least volatile compound studied (C_{16}) may not be adequate for many sampling situations. The capacity for XAD-2 becomes quite good at C_{13} and appears to retain material reasonably well down to a C_{10} volatility. The experiments on both Tenax-GC and XAD-2 show that the weight capacity is a function of input challenge level.

The weight capacity data obtained from the higher concentration challenge levels in these tables is plotted in Figure 18 vs. boiling point of the

Table 7

Specific Retention Volumes (Vg) of
Other Selected Pollutants on XAD-2

Compound	BP(°C)	Column Temp.(°C)	Vg*	$\log_{10}$Vg
Aroclor 1242	-	135	> 64,800	--
Pyrene	393	135	> 64,800	--
Agent Orange 2,4-D	317	135	∿ 60,500	∿ 4.82
2,4,5-T	356		⩾ 60,500	--
Vinylchloride monomer	-14	60	62	1.79

*each value is from a single experiment

Table 8

Steady State Challenge Capacity: XAD-2

Hydrocarbon	Condition	Conc. (mg/m^3)	$\log_{10}Vg(m\ell/g)$	Weight Capacity (mg/g)
n-octane	dry	9.2	4.13	0.09
n-octane	dry	10.2	4.56	0.25
n-octane	dry	11.4	4.18	0.15
n-octane	dry	26.2	4.44	0.57
n-decane	dry	10.9	4.99	0.49
n-decane	wet[1]	10.6	5.10	0.52
n-decane	dry	11.6	5.09	0.29
n-decane	dry	20.4	>5.1	>2.8
n-decane	dry	107	4.73	3.5
n-decane	wet[2]	102	4.85	6.5
n-tridecane	dry	110	-	>18
n-tridecane	dry	510	4.95	43
n-hexadecane	dry	1040	5.11	125

1. 16.7% RH

2. 13.4% RH

Table 9

Steady State Challenge Capacity: Tenax-GC

Hydrocarbon	Condition	Conc. (mg/m^3)	$Log_{10}Vg(m\ell/g)$	Weight Capacity (mg/g)
n-octane	dry	9.2	3.97	0.08
n-decane	dry	10.2	4.56	0.21
n-decane	dry	99.5	4.17	1.36
n-tridecane	dry	104	4.67	4.2
n-tridecane	wet[1]	110	4.59	3.5
n-hexadecane	dry	99.6	4.84	5.3
n-hexadecane	wet[2]	96.7	4.90	7.0
n-hexadecane	dry	491	4.48	12

1. 13% R.H.

2. 20% R.H.

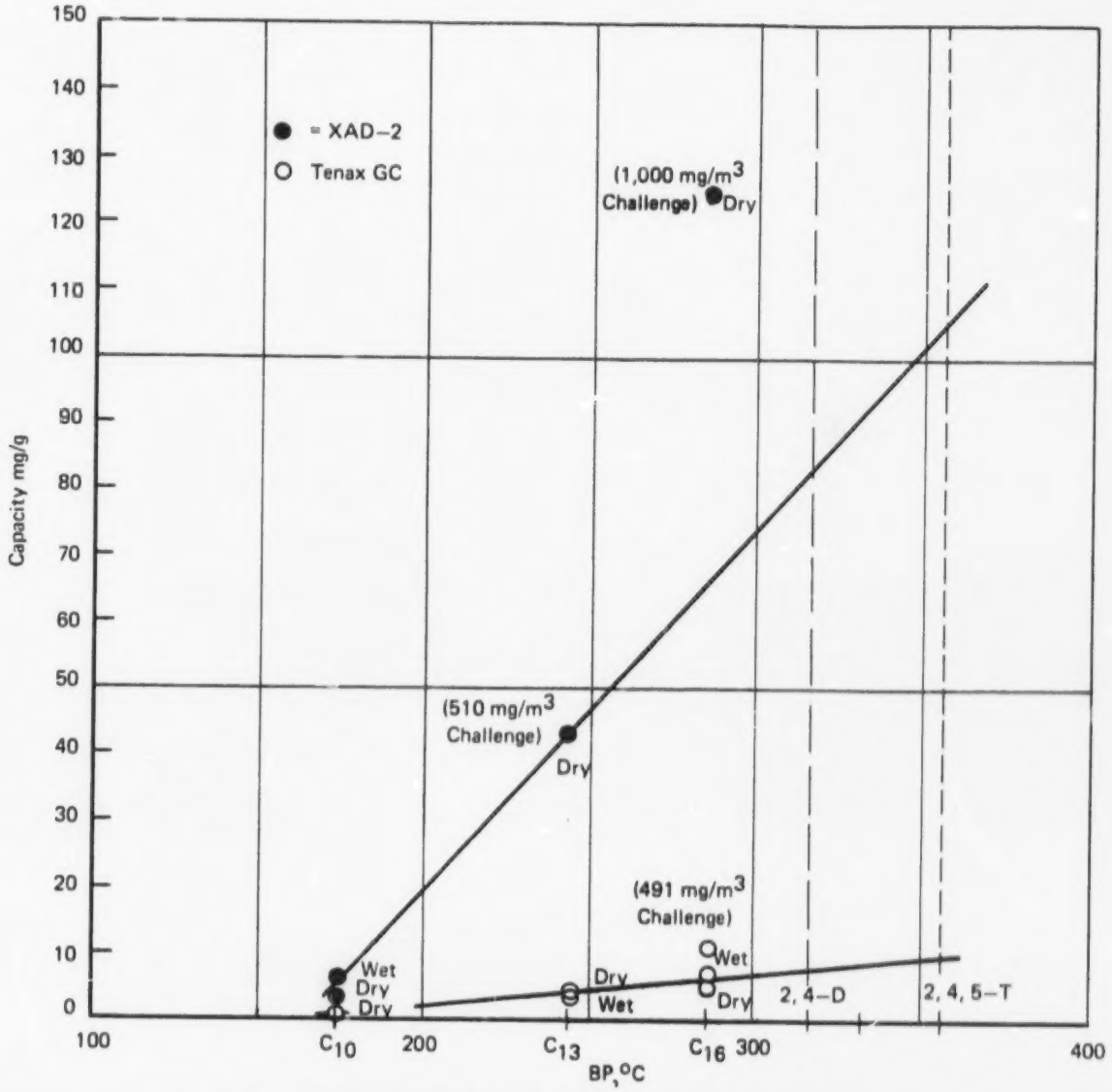

FIGURE 18 SORBENT RESIN CAPACITY VS. BP 100 mg/cu m CHALLENGE CONCENTRATION

compounds. A linear relationship appears to exist at least for the Tenax-GC where there is sufficient data at a single concentration. Comparable data at a single concentration does not exist for XAD-2 because breakthrough did not occur. Estimates may be made from the higher concentration level data for this resin. The boiling points of the Agent Orange species 2,4-D and 2,4,5-T have been indicated on this chart in order to extrapolate what the capacities of the resins might be for these species. Tenax-GC calculates to have a capacity of about 8 mg/g while XAD-2 projects to a capacity of greater than 100 mg/g.

Humidity does not appear to have any deleterious effect on the collection capacity. In fact it may improve the capacity. For Tenax-GC, the tridecane capacity was decreased by water, but the hexadecane capacity was increased. In the case of XAD-2 the capacity was increased in both cases (10 and 100 mg/cu m) in the presence of water. This effect might be rationalized in terms of the hydrocarbons having a higher affinity for the organic resins than the wet (now polar) air stream. The data do indicate that there is no significant interference in the physical adsorption process such as blocking of the pores. In a study on Tenax-GC published by Janak and coworkers[16] in 1974, they found no measurable effect of water on the retention of several compounds, even when using 100% relative humidity.

The experiments run on XAD-2 (Table 8) with both 10 and 20 mg/cu m challenge levels give similar Vg values indicating that Vg values taken from the 10 mg/cu m experiments are in the Henry's law region and provide a basis for comparison with the GC derived data. The data from both experiments available for direct comparison are given below.

	$\log_{10}$ Vg (mℓ/g)			
	XAD-2		Tenax-GC	
	GC	Steady State	GC	Steady State
Octane	4.65	4.2	4.05	4.0
Decane	(5.4)*	5.0	5.3	4.5

* extrapolated

Considering the marked difference in the experiments, the agreement between the Vg's derived from these two approaches is very good. On the average, the Vg's from the GC experiment are higher than those from the steady state apparatus. These data suggest that an average value of about 0.5 $\log_{10}$ Vg should be subtracted from the GC derived Vg's in order to provide a direct comparison with SASS or modified Method 5 train conditions.

Although many workers have found a constancy of Vg with gas velocity[17,18], the tenfold velocity difference between the GC and steady state experiments reported here may be the basis of the difference in Vg's between the two experiments. The GC experiment with its lower velocity has a greater likelihood of achieving true equilibrium. More recent studies by others[19,20] have shown some dependence of Vg on gas stream velocity. The effects have been attributed primarily to pore volume diffusion and gas-solid (or surface) interactions.

E. Applicability to Agent Orange Shipboard Incineration Tests

Part of the purpose of these experiments has been to relate the performance of the collection efficiency of the sorbent traps to the sampling associated with the Agent Orange shipboard incineration tests. Some relevant parameters for the Mathias III are

waste feed rate	65 metric tons/hour
exit gas flow	76.4 cu m/sec
exit velocity	0.5 m/sec
exit temperature	1200°C
excess air	19%

Table 10 shows some values calculated from these data for Agent Orange containing 50/50 2,4-D and 2,4,5-T and 3 ppm of TCDD. Assuming the destruction efficiencies indicated, then the data following in the table would be expected for emission rates. If the gas containing those concentrations were sampled by a Method 5 train or the SASS train under the conditions indicated, then the indicated quantities of material would be collected.

Collection efficiency for TCDD should not be a problem. However, very low quantities are expected, and there may be some problems in quantitative recovery for analysis. The amount of TCDD available could range anywhere from 1 to 240 µg.

The complete collection of the primary Agent Orange species could be a problem. If the incinerator is only operating at 99% efficiency, there could be 82 g of Agent Orange, plus other products, in the SASS train sorbent trap.

We do not know what the maximum resin weight capacities might be for Agent Orange at high challenge concentrations, but we can arrive at an upper and low limiting estimate. The steady state experiments shown in Figure 18 give a lower level estimate of about 10 mg/g for Tenax-GC and 100 mg/g for XAD-2 for the equilibrium capacity at low concentrations. An upper limit estimate of the trap capacity can be calculated assuming that, due to the low volatility of Agent Orange, the capacity is equal to the pore volume of the resin based on condensation and filling of the

Table 10

MATHIAS III - AGENT ORANGE BURN

	2, 4-D + 2, 4, 5-T			TCDD	
Destruction Efficiency	99%	99.9%	99.99%	99%	99.9%
Emission Rate, mg/cu m	2,400	240	24	0.007	0.0007
Quantities Collected, mg					
Method 5, 28 lpm (1 cfm) - 1 hr, 1.7 cu m	4,100	410	41	0.012	0.0012
SASS, 142 lpm (5 cfm) - 1 hr, 8.5 cu m	20,000	2,000	204	0.060	0.006
SASS, 142 lpm (5 cfm) - 4 hr, 34 cu m	82,000	8,200	820	0.24	0.024

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pores. The pore volumes are 0.85 cc/g for XAD-2 and 0.053 cc/g for Tenax-GC. The following estimate can then be arrived at for the SASS train sorbent trap capacity for Agent Orange

Resin	SASS Sorbent Trap Resin Quantity (g)	Agent Orange Trapping Capacity	
		Steady State Lower Limit (g)	Pore Volume* Upper Limit (g)
Tenax-GC	57	0.6	3
XAD-2	130	13	110

* Assuming unit density for Agent Orange

By comparison of these values with the data in Table 10, one can see that Tenax-GC would only be acceptable for the most efficient burn. XAD-2 would have sufficient capacity for all of the conditions listed. Using XAD-2 in the SASS sorbent modules would give a maximum holding capacity for Agent Orange of 100 g when sampling from a high effluent concentration. When sampling at low effluent Agent Orange concentrations, the capacity would be 13 g. If the destruction efficiency from Agent Orange was 99.99%, corresponding to a stack concentration of 24 mg/cu m, it would be possible to sample 540 cu m or for up to 64 hours at the SASS sampling rate of 5 cfm (142 liters/minute) before exceeding the trap capacity. These values will be altered as other species compete for the adsorption capacity of the resin.

F. Recovery of TCDD

Because of its low volatility, collection of tetrachlorodibenzodioxin (TCDD) on the sorbent resins will not be a problem. However, because the potential quantities involved in the incineration tests are so small, quantitative recovery could be a problem. In order to investigate this issue, XAD-2 traps were spiked with TCDD and its recovery determined.

The potential quantity of TCDD to be collected in the shipboard tests could range from 1 - 240 µg (Table 10). XAD-2 traps (Figure 11) containing 40 g of XAD-2 were spiked in duplicate with 5 µg and 50 µg of TCDD. The traps were then extracted overnight with pentane in a continuous extractor. The pentane solutions were concentrated and analyzed by GC. The GC studies were done using a Ni-63 electron capture detector and properly prepared calibration curve. The glass column was a 10% OV-17 on 100/120 Supelcoport, 2.5 ft. x 1/8 i.d., operating at 200°C.

The results were as follows:

TCDD Added (µg)	Recovered (µg)	% Recovery
5.0	3.4, 4.4	68,88
50	32,33	64,66

Based upon the average of these results, the recovery of TCDD should be at least 65%. Recovery might actually be expected to be higher in the tests where the resin would be loaded with Agent Orange and other species which would help in co-eluting the TCDD from the resin.

IV. CONCLUSIONS AND RECOMMENDATIONS

XAD-2 has been shown to be more efficient than Tenax-GC as a collector for use in the SASS train sorbent trap. The volumetric breakthrough capacity for low input challenge levels is about three times greater for XAD-2 than for Tenax-GC. The weight capacity breakthrough is about ten times greater for XAD-2 than Tenax-GC, as determined from the steady state challenge experiments at high concentrations.

The volumetric capacity (Vg) of both XAD-2 and Tenax-GC shows a regular dependence on the volatility (boiling point) of the pollutant. There is an indication that this relationship may be different for compounds of different polarity classes.

A SASS train sorbent trap operating for four hours will collect all materials boiling above 190°C ($> C_{10}$) when using XAD-2 and above 240°C ($> C_{13}$) when using Tenax-GC. Both materials will efficiently collect POM's, PCB's and Agent Orange initially, but the XAD-2 will have a much greater capacity for these materials. Neither material will be adequate in collecting vinyl chloride monomer.

The effort associated with this task has enabled the beginning of only some of the systematic studies which are needed for a complete quantitative understanding of the sorbent trap behavior. Several areas should continue to be explored for further understanding. Some of these are:

- Establish volumetric capacity (Vg) - volatility (boiling point) relationships for various compound classes.
- Develop the quantitative relationship between volumetric capacity derived from the two different types of experiments: elution (gas chromatography) and frontal (steady state) analysis.
- Determine the collection efficiency of sorbent traps for aerosols (formed by cooling in the heat exchanger).
- Determine compound recovery as a function of class type and concentration.
- Completely characterize resin blanks for possible interferences in each of the analytical steps used to determine pollutants collected by the traps.

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Appendix A

Individual Specific Retention Volume (Vg) Data

Specific Retention Volume (ml/g)

XAD-2

135°C

Compound	Vg				$\bar{V}g$	S.D.
Hexane	47	38			43	6.4
Benzene	56	45	47	47	49	4.9
Octane	319	249	252	263	271	32.7
Decane	2122	1663	1746	1818	1837	200
Phenol	556	442	449	460	477	53.4
Aniline	643	502	552		566	71.5
Dichlorobenzene	1080	834	883	898	924	108
Napthlene	4535	3502	3602	3802	3860	467
Mass Packing (g)	0.7326	0.7506	0.7113	0.7411		

Specific Retention Volume (ml/g)

XAD-2

96°C

Compound	Vg				Vg	S.D.
Hexane	290	213	-	-	252	54.4
Benzene	328	258	227	227	273	42.4
Octane	3299	2862	2519	3032	2928	327
Decane	> 16,000	-	-	-	--	--
Phenol	5614	5009	4099	5246	4992	645
Aniline	6019	5461	4889	-	5456	565
Napthalene	-	-	-	9851	9851	--
Mass Packing (g)	0.7326	0.7506	0.7113	0.7411		

Specific Retention Volume (ml/g)

TENAX GC

135°C

Compound	Vg			$\overline{Vg}$	S.D.
Hexane	15	11	-	13	2.8
Benzene	26	25	30	27	2.6
Octane	49	56	64	56	7.5
Decane	275	324	324	308	28.3
Dodecane	1355	1728	-	1542	264
Tridecane	2907		3754	3331	599
Phenol	289	315	288	297	15.3
Aniline	398	438	-	418	28.3
Dichlorobenzene	482	537	474	498	34.3
Napthalene	1846	2067	1685	1866	192
Mass Packing (g)	0.3611	0.3064	0.3054	0.3100	

Specific Retention Volume (ml/g)

TENAX GC

96°C

Compound	Vg				$\bar{V}_g$	S.D.
Benzene	149	170	130	175	156	20.7
Octane	641		633	703	659	38.3
Decane	6497	6090	6495	6895	6494	329
Phenol	3092	3137	2931	3140	3075	98.5
Aniline	4443	4521	4180		4381	179
Dichlorobenzene	5872	6136	5939	6128	6019	134
Mass Packing (g)	0.3611	0.3064	0.3054	0.3100		

Appendix B

Relative Specific Retention Volumes (Vg) on Chromosorb 101
Vg Relative to Benzene at 190°C

Name	BP(°C)	$Vg/Vg(C_6H_6)$	$\log_{10}$ rel Vg
Benzene	80	1.00	0.000
Toluene	111	1.86	0.270
Ethylbenzene	136	3.48	0.542
o-Xylene	144	3.94	0.595
m-Xylene	139	3.36	0.526
p-Xylene	138	3.27	0.515
Propylbenzene	159	5.26	0.721
Mesitylene	165	5.76	0.760
n-Butylbenzene	183	8.58	0.933
Durene	190	11.75	1.070
Chlorobenzene	132	3.31	0.520
o-Dichlorobenzene	180	10.35	1.015
m-Dichlorobenzene	172	8.41	0.925
p-Dichlorobenzene	174	8.41	0.925
1,2,4-Trichlorobenzene	214	18.35	1.264
1,2,4,5-Tetrachlorobenzene	243	47.7	1.679
Bromobenzene	155	6.86	0.836
m-Dibromobenzene	220	26.3	1.420
p-Dibromobenzene	218	27.4	1.438
Iodobenzene	188	12.8	1.107
Phenol	182	7.16	0.855
Pyrocatechol	246	31.2	1.494
Resorcinol	276	58.7	1.769
Hydroquinone	285	43.2	1.635
o-Chlorophenol	175	7.9	0.898
p-Chlorophenol	217	24.8	1.394

Appendix B - continued

Relative Specific Retention Volumes (Vg) on Chromosorb 101
Vg Relative to Benzene at 190°C

Name	BP(°C)	$Vg/Vg(C_6H_6)$	$\log_{10}$ rel Vg
2,4,6-Trichlorophenol	246	69.9	1.844
o-Cresol	191	12.25	1.088
m-Cresol	203	14.0	1.146
p-Cresol	202	13.85	1.141
2,3-Dimethylphenol	218	23.5	1.371
2,5-Dimethylphenol	212	19.55	1.291
2,4,6-Trimethylphenol	221	27.7	1.442
2,4,5-Trimethylphenol	231	38.4	1.584
2,3,4-Trimethylphenol	?	46.8	1.670
o-Propylphenol	223	38.7	1.588
Aniline	184	10.90	1.037
Nitrobenzene	211	18.95	1.278
m-Dinitrobenzene	301	112.0	2.049
o-Nitrotoluene	222	22.4	1.350
m-Nitrotoluene	233	27.2	1.435

Source: T.N. Gvosdovich, A.V. Kiselev and Y.I. Yashiu, Chromatographia 6, 179 (1973).